



LECTURES ON THE PRINCIPLE  
OF SYMMETRY.



LECTURES  
ON  
THE PRINCIPLE OF SYMMETRY  
AND  
ITS APPLICATIONS IN ALL  
NATURAL SCIENCES

BY  
F. M. JAEGER, Ph. D.  
PROFESSOR OF INORGANIC AND PHYSICAL CHEMISTRY  
IN THE UNIVERSITY OF GRONINGEN, HOLLAND.

WITH 170 DIAGRAMS.

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To

William Jackson Pope, M.A., F.R.S.

Professor of Organic Chemistry in the University of Cambridge.

this Book

is dedicated

in admiration of his very important work  
in this field of research

by

The Author.



## P R E F A C E.

The present book originated in a series of lectures delivered by the author during the winter and spring 1916—1917 at the University of Groningen. The matter of these was afterwards augmented by the contents of some addresses held about ten years ago at the University of Amsterdam, and by that of some others delivered in various places in this country and in America. In response to a desire, repeatedly expressed by some of his friends, the author has finally resolved to publish these lectures in bookform. Only in occasional passages, however, does it betray this devious course of development.

The aim of the writer in publishing this volume is by no means to give an exhaustive "treatise" of the general doctrine of symmetry. His purpose is merely to draw the attention of students of mathematics and natural philosophy in general, to a principle of which the significance in the morphological description of objects, as well as in the definition of chemical and physical phenomena is gradually becoming more and more evident in every domain of research.

The complete deduction of the properties and mathematical character of symmetrical systems has been so ably treated by a number of the best authors, and in such various ways, that there is small chance of new points of view being found in the future. Moreover the results have from time to time been summarised in a

number of papers which are accessible in all greater libraries to every one who wishes to go further into these subjects. Hence it appeared needless to repeat such an exhaustive treatment of these questions in this book, which is intended rather to fascinate the more vivid and impulsive imagination of the observer and experimenter, than to satisfy the more slowly working and quiet mind of the mathematician. The whole treatment of the necessary theorems and deductions of the general doctrine of symmetry has therefore been condensed into four chapters of this book, in which at the same time even its applications to morphology have been inserted. Notwithstanding this the author hopes that he has given a sufficiently complete deduction of the theorems, so that even for those students who wish to go further into the mathematical theory itself, the general way of reasoning may be found clearly indicated.

After seriously testing the methods of argumentation hitherto elaborated, the writer has in many places finally adopted that of Schoenflies, chiefly because in his opinion it offers, from a teaching standpoint, undeniable advantages over the often not less happy and concise ways of treating the problem employed by authors such as Von Fedorow, Wulff, Viola, Barlow, Boldyrew, and others. However many alterations and extensions have been occasionally made, chiefly with the intention of keeping the deduction as general as possible, even for cases which are of no special crystallographical interest, though doubtless important for biologists. The author is convinced that Möbius' definition of symmetrical figures has some logical advantages above the somewhat dualistic definition of Von Fedorow and Schoenflies adopted here; and also that, from a mathematical standpoint, the methods of demonstration of Wulff and Viola, and more especially that of Boldyrew, may perhaps be considered more homogeneous. But he is convinced also that confusion is more readily created in the mind of students of these subjects, when all symmetry-properties are reduced to mere "reflections" in planes of different functions, than when the "axial symmetry" is considered as well. Attention is however occasionally

drawn to several theses demonstrated by the authors last named, and their importance for certain purposes has in such cases been indicated as clearly as possible.

Moreover abundant references to literature are made throughout, so that the student who wishes to refer to or read the various authors in their respective languages, will find his labour appreciably facilitated.

The examples, chosen from biological sciences and more especially from morphological descriptions, for illustrating the applicability of the symmetry-principle in this province, have no claim to absolute correctness. It is in general impossible for a chemist or physicist to judge the exactness of such descriptions in morphology by means of drawings only, unless he has by chance gone into these subjects in detail. The instances mentioned must be considered as somewhat preliminary, intended only to prove the possibility of a form-description based upon the principle of symmetry. However it will not give much trouble to biologists to find the right symmetry of each object, if only the general principles are once clearly understood by them. The author will be grateful for suggestions offered by his colleagues in a kindly spirit.

When the present work was almost finished, a copy of a little book in the Russian language from the hand of Professor G. W. Wulff: "Symmetry and its Manifestations in Nature", came into the author's possession. It contains a short review of four lectures delivered by the writer in 1907, at the request of the Society for Popular University Instruction in Moscow. As the range and design of these lectures are obviously quite different from those of the present volume, there was no reason for the author to consider his book as superfluous and to give up its publication.

If the contents should instigate our students of natural philosophy and our future investigators to some new experiments or to any applications in the different fields of research, the writer would think himself amply rewarded for the work done in composing this book.

In conclusion, it is my pleasant duty to express my sincere thanks to the Board of Trustees of the Groningen University Fund and to the Directors of the Utrecht Society for Science and Arts, who by their support have rendered possible the publication of this volume in its present form at such an unfavorable time; as well as to the publisher for the care he has bestowed on the printing, and the attractive garb he has given to the book.

F. M. JAEGER.

*Groningen, Holland, May 1917.*

*Laboratory for Inorganic and Physical Chemistry  
of the University.*

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## CHAPTER I.

*Introductory Remarks. — The Symmetry-Principle in General.  
Its Aesthetic Value. — Definition of Symmetrical Figures.  
Symmetry-Properties and Symmetry-Character.*

γὰρ οὐκ ἔστις ἡ γεωμετρικὴ γνῶσις ἔστ  
P l a t o, Pol. 7.527.b.

§ 1. Of the numerous theories suggested to explain natural phenomena, such have proved particularly efficient, as allow of *mathematical* treatment, and therefore are especially suited for the outlining of repeatedly observed facts in their mutual dependence.

Not before such a summarising mathematical description of the most obvious features in the relationship of the natural phenomena considered, or between groups of them, has been performed as concisely as possible, — can we claim to have really understood the observed facts in their logical connections.

In this mathematical outlining of nature, human science makes use of a number of fundamental notions and principles which, commonly after a long period of error or opposition, have been generally accepted in the end. The methods of mathematical physics with its classical mechanics, as well as its recent views on electromagnetics, are well-known illustrations of this. Such fundamental notions are at last adopted generally, if they prove to be extremely effective in the further theoretical development and schematising of natural phenomena.

Among ideas of this kind playing an important rôle in modern science, *the principle of symmetry* may certainly be considered as one of the most remarkable and interesting.

The idea of symmetry resulted originally from the study of geometrical forms and the observation of natural objects. Now, after its mathematical formulation has been elaborated, and all the conclusions drawn from it have been systematically gathered into what is commonly named "the general doctrine of symmetry", — the said principle finds application in those fields of natural science also, such as e.g. physics and chemistry, where geometrical properties are taken into account commonly in cases in which the dimensions considered will most probably for ever remain beyond the scope of direct observation.

§ 2. By the use of the word "symmetry" in the study of forms

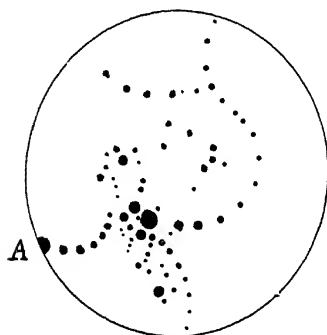


Fig. 1.

and figures it is intended to draw attention to some *geometrical regularity*, to a certain *process of repetition*<sup>1)</sup> which manifests itself in the external habit of the figure considered. It is well known, that there is implied a powerful *aesthetic factor*<sup>2)</sup> in the mere *repetition* of a visual impression, and it is in this, that symmetry became an important *aesthetic principle* in decorative art and architecture.

In *Fig. 1.* a perfectly arbitrary complex of large and small black dots is represented. The figure formed by them does not make any particular impression on the observer. If, however, this meaningless figure is repeated several times by rotating it round an axis *A*, perpendicular to the plane of the figure, each time through an

<sup>1)</sup> The Greek word *συμμετρία* signifies: right proportion, evenness, measurableness, dimension; *σύμμετρος* is: uniform, suitable, proportional, measured-off; and likewise the adverb *συμμέτρως* has the meaning: keeping the due medium between. Democritus e.g. speaks of: *ἐνυμμετρίῳ βίῳ* for: the equableness of life; etc,

<sup>2)</sup> The significance of symmetry as an aesthetic principle was already brought into the fore by the ancients. Thus e.g. Plotinos in his famous book on Aesthetics, in the first Ennead, liber 6, cap. 1, says: "Now almost by all persons it is maintained, that it is the *symmetry* of the different parts with respect to each other, and the beautiful colour, which produce *beauty* for visual observation; and for those as well for the common intellect *beauty* is identical with *symmetry* and being shaped after fixed proportions."

angle of  $72^\circ$ , the pattern of *fig. 2* will be produced. This pattern, on the other hand, makes an undeniable "aesthetic" impression. In the same way the particular effect of the patterns of wallpapers, of drapery-, or dress-materials, is produced, and also that of the symmetrical ornaments which are met with more particularly in classic architecture.

In the well-known *mirror-calidoscopes*, the surprising and very beautiful effects are obtained by means of the repeated reflection in regularly arranged little mirrors.

A number of insignificant pieces of coloured glass which are thrown together by mere chance, will however now seem to be purposely arranged and combined in beautifully shaped, coloured patterns. Here also the aesthetic action is caused exclusively by the regular repetition of the

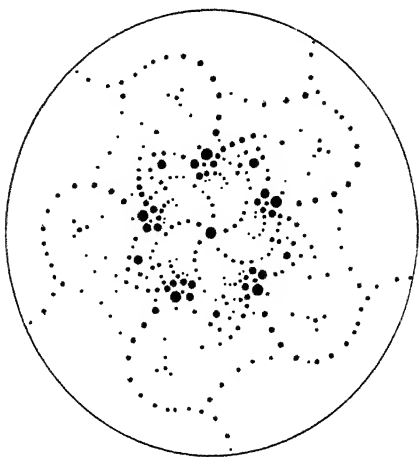


Fig. 2.

same arbitrary figure. The splendour and fascinating beauty of a great number of living creatures: *radiolaries*, *medusae*, *diatomeae*, *corals*, *star-fishes*, of innumerable *flowers*; that of the brilliant forms of many *crystals* and of the figures produced by *vibrating membranes* (eidophone) or metalplates (Chladni), etc.<sup>1)</sup> — are in each case caused by the mere action of symmetrical repetition. Indeed, the principle of form-symmetry in its strict formulation, has been neglected too long already\* in the morphological and systematical description of the biological sciences; or at least: its scanty applications have been too rudimentary and insufficient in almost all cases. In this respect it is most necessary that the obsolete and unwieldy definitions of form still in vogue

<sup>1)</sup> Vid. Newton, Harmonic Vibrations. Remarkable symmetrical figures can be obtained e.g. with J. Goold's elliptic pendulum.

in these sciences, should be finally abandoned for a rational system of description, in which the doctrine of symmetry is the trustworthy guide.

For our purpose it is only necessary for the moment to keep in mind that the "symmetry" of a figure consists in some regular repetition of definite parts of it. Thus such figures can be made to coincide with themselves in several ways, either by superimposing or by some other operation.

§ 3. With respect to the *aesthetic* value<sup>1)</sup> of the symmetry-principle some few suggestions may be made here. The aesthetic action of symmetrical arrangement is really established beyond all doubt. Now E. Mach. (*Pop. Wiss. Vorlesungen*. (1903), p. 100) has drawn attention to the remarkable fact that the symmetry of a figure with respect to a single plane, will immediately be noticed, if the plane of symmetry is a vertical one; that in the event of its position being horizontal, however, the symmetry of the figure does not make a very strong impression: we can walk for many hours by the side of a lake, before our attention is drawn to the fact that the image in the water is the replica of the scenery itself. Vertical bilateral symmetry appears to be the one naturally adapted to us, while apparently horizontal is almost imperceptible to the observer. Mach tries to give an explanation of this fact by drawing attention to the other, that our visual apparatus itself possesses a vertical plane of symmetry. The right and the left eye are in their internal structure each other's mirror-images: the function of the one can therefore *not* be substituted for that of the other, as appears if one transposes the pictures of a stereoscopic photo. If we now look through the stereoscope, a strange world is observed, in which concave and convex are interchanged, and in which all that should stand out, now recedes into the background, and vice versa. The impression of a vertical symmetrical figure thus would result from the circumstance that the right eye sees the right part of the figure in just the same way as the left eye sees the left part of it. The effect of vertical symmetry of this kind would really be an *intensifying of the single impression*, and would therefore be immediately noticed by us.

However the question seems to be much more complicated than

<sup>1)</sup> Cf. H. N. Day, *Aesthetics*, p. 76, § 72, (1872): "Akin to this beauty of proportion is the beauty of symmetry", etc.

Mach supposes. For it is well-known, that in the case of persons born blind too, often a rather developed sense for symmetry has been observed, which evidently seems to have developed in connection with their sense for touch. It thus appears highly probable that the peculiar preference for vertical symmetry is intimately connected with the movement of the extremities, and would thus finally be explained by the vertical symmetry of the body as a whole. Mach himself brings forward against his own explanation of the above mentioned preference for vertical symmetrical figures, an argument which seems unjustified in this connection, by pointing to the fact that our hearing-apparatus too has a vertical plane of symmetry, and notwithstanding this the melody and its "mirror-image", as played on a suitably arranged piano, will absolutely differ from each other acoustically. For the right ear does not hear the sound-waves in any way other than the left ear does, so that the comparison with the case of visual observation is evidently a wrong one.

However, the explanation which connects the established preference for vertical symmetrical figures with the vertical symmetry of the body and the movement of the extremities, cannot be considered to give a final explanation of the aesthetic action of the symmetrical arrangement in general either. In *fig 2* on page 3 we have a symmetrical figure, *which does not possess any planes of symmetry whatever*; notwithstanding this, the aesthetic impression is undeniably present here. This leads to the conclusion that this action is *merely* caused by the fact of the *regular repetition* as such. In my opinion the influence of this is a double one. For in the first place this repetition helps to *intensify* the primary visual impression, even if this be only an indifferent one, so that the rather feeble psychological reaction of it now comes into consciousness with much sharper outlines. And secondly, the final impression will correspond with the one which the observer inarbitrarily *expected* beforehand, from his notion of the regular repetition of the primary impression. The symmetrical arrangement thus appears to represent one of the numerous means by which mental action is facilitated, and an economy of energy is obtained. However I have mentioned these views here only as an instigation to perhaps better ones, — not because I think they bring a final explanation of this complicated matter.<sup>1)</sup>

<sup>1)</sup> Similar views on the aesthetic action of symmetrical arrangement have

§ 4. In this connection it seems not out of place perhaps, to make some few remarks about the question, in how far we can really speak of true "symmetry" with respect to the geometrical properties of objects observed in nature? For it is certainly true that we attribute to every animal, to every flower or leaf or crystal, a characteristic external form. Everyone of us can at a glance tell what the difference is between an *oak*-leaf and that of a *poplar*, or between the octahedral *alum*-crystal and that of *quartz*.

But detailed observation soon teaches us that two oak-leaves or two poplar-leaves, two alum-, or two quartz-crystals, are *never* absolutely identical; and that properly speaking, an undisturbed and invariable regularity of form, as the result of an accurate repetition of definite parts of the object, can never be met with. Thus the one half of the oak-leaf appears never to be precisely the same as the other half; the alum-crystal never has twelve accurately equal angles, etc. Notwithstanding this variability however, we never hesitate in recognising a given leaf as being that of an oak-tree, nor a given alum-crystal as being an octahedron. The reason of this is, that as a consequence of our frequent observation of these objects, we have formed an *ideal* image of the completely developed and perfect leaf or crystal, by abstraction of all that is accidental; and we have learned to consider the observed forms as only more or less perfect approximations to that ideal form. For we are convinced, that if circumstances are more and more favorable to free and undisturbed development during the growth of the oak-leaf or the alum-crystal, we shall find a closer approximation also to the standard-form mentioned. It is only to this imaginary standard-form, that we can extend our considerations regarding the symmetry-principle; it is again an *idealistic scheme* of nature only, to which these mathematical reasonings are to be applied. In common parlance we say that

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also been brought forward and formulated by G. Heymans: *Zeits. f. Psychologie und Physiologie der Sinnesorgane*, 11. p. 333, 335, 339, 340. (1896). The question is here considered from the general viewpoint of the adaptation of attention to subsequent observation, as a consequence of the psychological preparedness for that coming impression, when its special nature is qualitatively and quantitatively on the same level with what was expected in imagination. If this be the case, according to this author, a feeling of comfort and delight will be produced, because of the easy assimilation of the real occurrence to the analogous expectation already present in our mind.

the leaf of the oak or the poplar is "intended by nature" to be bilaterally symmetrical, or that the crystals of alum "of their own nature" represent octahedra. But this only bears upon a world of abstraction, the intellectual image of this imperfect visible world. With respect to our mathematical scheme of forms in natural objects, we are indeed still very close to the idealism of a Plato or Aristotle. It may here be mentioned also that only in some cases, e.g. in that of crystalline matter, we have succeeded in giving a rational explanation of the connection between the internal structure and the characteristic external form of a thing. But as regards living organisms, it can hardly be hoped within a measurable space of time to connect their intimate nature with the constant occurrence of their typical external forms in any direct way, although that form is typical in no less a degree of them, than it is of crystalline substances.

In every case it must be remembered here that in the following paragraphs our views regarding the principle of symmetry can only be applied to objects in the sense mentioned; only the *ideal* forms, the "standards" of them, are taken into account, to which the observed forms should more and more closely approach, as the circumstances during the growth of these natural objects are becoming more favorable.

§ 5. It has already been said (§ 2), that symmetrical figures can be brought to self-coincidence in several ways; they are equal to themselves in more than one respect. Indeed *fig. 2* represents such a "symmetrical" figure, because it takes a new position always congruent with the initial one, when it is repeatedly rotated through an angle of  $72^\circ$  round the axis *A* before mentioned; and this can be done five times in the same direction. After the fifth motion the figure is again in exactly the same position as it was at the beginning. It seems to be adequate in this case to define the typical symmetry of the figure by these characteristic rotations. Although in the case considered this will really appear to be justified, we have however still to modify our definition of symmetrical figures with respect to another particular, before it can seem complete. In *fig. 3* a complex of dots, just like those in *fig. 2*, is drawn in the same mutual positions and of the same magnitude; the figure evidently possesses the same symmetry as the original one; but notwithstanding all details and properties are the same as in *fig. 2*,



it will appear to be impossible now to move the figure in its own plane<sup>1)</sup> in such a way, as to make it coincide with *fig. 2*. We can, however, obtain *fig. 2* from *fig. 3* by reflecting the last one in a mirror *S*, placed perpendicular to the plane of the drawing; the mirror-image of *fig. 3* now obtained, is really *congruent* with *fig. 2* itself, and it can now be brought into coincidence with it by mere shifting and rotating. Because of this relation, we say that

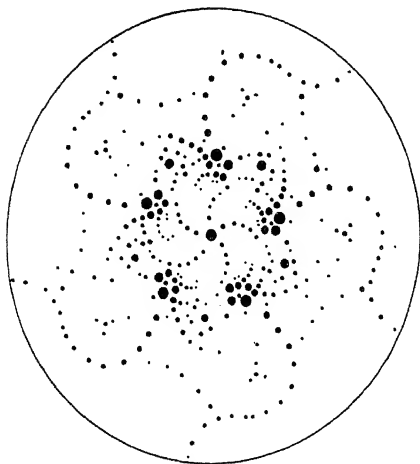


Fig. 3.

the plane figures 2 and 3 are each other's *mirror-images*. Such mirror-images, although built up by the same geometrical elements, are evidently *not* congruent, and they can never be made to coincide by mere movement.

The same is observed in tri-dimensional space: there are numerous objects, e. g. "right" and "left" hand or foot, screw-threads and tendrils,

etc., — which are wellknown instances of this kind. They are related to each other as mirror-images, and they can *never* be brought to coincidence by mere rotations or shifting. Only the "mirror-image" of each of them will coincide with the other object itself in the way described above. This is commonly expressed by saying that the right and left extrimities, or the screw-threads, etc. are objects which are *different from their mirror-images*.

It must however be kept in mind that a number of objects are not at all different from their mirror-images: our own body is a good example of this. If we look into a mirror, we soon come to the conviction that the mirror-image of our body is really *congruent*

<sup>1)</sup>. The condition that this two-dimensional figure remains *in its own plane* during its motions, is essential in this mode of argument. In a tri-dimensional space the figure would be brought to coincidence with itself by a mere rotation through  $180^\circ$  round an axis situated in its own plane.

with it. Indeed, if we imagine the mirror-image rotated round a vertical axis through  $180^\circ$ , and then shifted parallel to itself until it is just as far in front of the mirror, as it is now behind it, the image will appear to coincide absolutely with the body itself. Because we have altered nothing of the original mirror-image during this operation, the coincidence of both proves undeniably that the human body is an object which does *not* differ from its mirror-image. We can easily test this moreover, if we think for a moment of the body as reflected in a vertical mirror-plane, coinciding with the meridian plane, which would divide the body in two symmetrical halves. These parts would appear to be each others mirror-images also, but the body as a *whole* is just the same as the original object. Afterwards we shall see that just *because* this meridian plane is characteristic of the special symmetry of the human body, this has the property of being congruent with its mirror-image.<sup>1)</sup>

Another instance of such a figure which is in different ways similar to its mirror-image, is the *cube* (fig. 4).

From fig. 4 it appears, that the cube, reflected in each plane  $abcd$  brought through two opposite edges, will coincide with its original position; and evidently there are *six* of such mirror-planes present. In the same way the cube will coincide with itself if reflected at one of the *three* possible planes

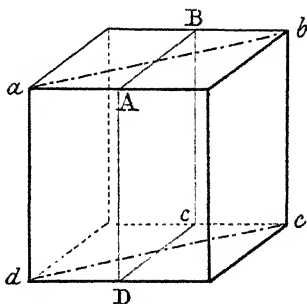


Fig. 4.

<sup>1)</sup> In this connection it may be mentioned that the difference between the two kinds of operations here considered, by which a figure is brought into coincidence either with itself or with its mirror-image, has a simple analytical expression too. For in reality we are dealing here only with ordinary orthogonal substitutions of coordinates. Now if the position of the new coordinate-axes  $X', Y', Z'$ , with respect to the old ones  $X, Y, Z$  is given by nine directional cosines  $C_{xx'}, C_{yx'}, C_{zx'}$ , etc., the relations  $C_{xx'}^2 + C_{yx'}^2 + C_{zx'}^2 = 1$  and  $C_{xx'} \cdot C_{xy'} + C_{yx'} \cdot C_{yy'} + C_{zx'} \cdot C_{zy'} = 0$  etc., have always validity. From this it is readily seen that the *square* of the determinant formed from these nine cosines, must have the value  $= 1$ . And from this relation:  $\Delta^2 = 1$ , it follows, that  $\Delta$  itself can be  $+1$  or  $-1$ . The case of  $\Delta = +1$  corresponds to the transformation of the system to a position in which it remains congruent with itself; the case:  $\Delta = -1$  however, to that in which it is the mirror-image of the initial system.

like  $ABCD$ . The cube is thus a figure, which in *nine* different ways is equal to its mirror-image. On the other hand, if (*fig. 5*) an *irregular tetrahedron*  $ABCD$  is taken, it is easily seen to be *different* from its mirror-image  $A'B'C'D'$ . Such a tetrahedron therefore is an instance of a figure, which is in *no* way equal to its mirror-image.

§ 6. We have dwelt somewhat long on this matter, because in the beginning it appears often difficult to obtain a complete and clear insight into these relations which on the other hand must be considered as of fundamental significance for the following. —

Now there are innumerable stereometrical figures which are similar to themselves as mirror-images: the cube, the octahedron, the cone, etc., are all instances of this kind. They all possess a

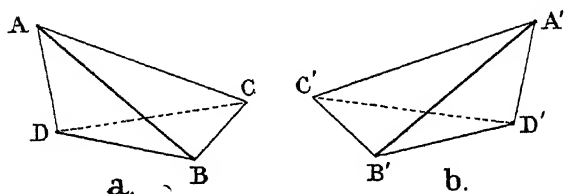


Fig. 5.

property which *fig. 5*, and *fig. 2* and *3*, if considered in their own plane, evidently lack. However, figures such as *fig. 2* or *3*, are surely "symmetrical" figures, and à fortiori, or at least for the same reason, the figures mentioned above must be called "symmetrical" ones too.

Therefore our previous definition of a "symmetrical figure" needs an extension in such a way, that we say: *symmetrical figures are such as are similar to themselves or to their mirror-images in more than one way.*<sup>1)</sup> In more than *one* way: for every figure is at least equal to itself by mere *identity*.

<sup>1)</sup> Indeed, there is a dualistic character in this definition, although it is quite sufficient for the complete mathematical deduction of all possible symmetrical systems, as Von Fedorow and Schoenflies have demonstrated. The old definition of Möbius is free from this dualism. It says: „Zwei Figuren heissen einander gleich und ähnlich, wenn jedem Punkte der einen Figur ein Punkt der anderen dergestalt entspricht, dass der gegenseitige Abstand je zweier Punkte der einen Figur, dem gegenseitigen Abstände der zwei entsprechenden Punkte der anderen Figur, gleich ist. Es gibt aber Figuren, welche sich selbst auf mehr als eine Art gleich und ähnlich sind; . . . solche Figuren sollen *symmetrisch* genannt

The different ways in which the congruency mentioned appears, determines the *symmetry-properties* characteristic for the stereometrical figure, and with them, the whole *symmetry-character* of it is given at the same time.

The complete set of symmetry-properties of every figure must thus be found out, before we can say what its particular symmetry-character really is. As we shall see later, however, not every arbitrary combination of such symmetry-properties can occur in any special case; if present together, they are evidently in some way connected and dependent of each other. In the next chapter, therefore, we shall see in what way symmetry-properties can be generally defined, and what is the special mutual dependency of them, if more of them are simultaneously present.

werden". Indeed, reflection in a mirror will preserve the original relations and distances of the different points to each other also in the mirror-image. This can easily be demonstrated.

## CHAPTER II.

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*General Considerations on the Change of Position of stereometrical Figures. — Characteristic Motions. — Figures and their Mirror-images. — Reflection and Inversion. — Finite and Infinite Figures. — Symmetry-Properties, Symmetry-Elements of the First and Second Order. Euler's Theorem. — Deduction of Symmetry-Character as a Mathematical Problem. — Geometrical Centre of Finite Figures. — Periods of Axes of the First, and of the Second Order. — Special Cases. — Repeated Reflections. — General Demonstration of the Symmetry-Relations.*

§ 1. If a stereometrical figure  $F$  be brought from its original position in space  $S_1$  into a different position  $S_2$ , two cases will be distinguished. The first case is, that the transition from  $S_1$  to  $S_2$ , can be made by means of a *motion*, i. e. by a *translation* (a shift parallel to itself), by *rotation*, or by *helicoidal motion*, this being a combination of the two former. In the positions  $S_1$  and  $S_2$ , the figure thus remains congruent with itself. This could also be regarded, as if two congruent figures  $F$  were compared, but in two different positions  $S_1$  and  $S_2$ . As a corollary therefore it must always be possible to bring two congruent figures  $F$  into coincidence by *mere motions* if they are in different positions in space.

Now we will suppose that the figure  $F$  is a symmetrical one, in the sense of our definition in the previous chapter. Then it will always be possible to make such a choice of the motions mentioned, that the figure can be brought from its successive positions  $S_2, S_3, S_4$ , etc., to self-coincidence and in its original place in space by *mere translations*. If this is the case, we will call the motions performed as *characteristic* of the particular symmetry of the figure  $F$ .

An example will make this clear.

Let  $A$  (fig. 6) be a cube, the corners of which for the sake of

clearness and reference, are numbered 1 to 8. Let us moreover take an arbitrary point  $P$  in space, outside the cube  $A$ , and draw a straight line  $LL'$  through it parallel to one of the four upright edges of the cube. If now  $A$  be revolved round the axis  $LL'$  through angles of  $90^\circ$ ,  $2 \times 90^\circ$ ,  $3 \times 90^\circ$ , etc., the cube  $A$  comes successively into the positions  $B$ ,  $C$ ,  $D$ , which positions differ from  $A$ , as the numbers at the corners clearly show. Because the cube now has a special symmetry of its own however, the figures  $B$ ,  $C$ , and  $D$ , can be made to coincide eventually with

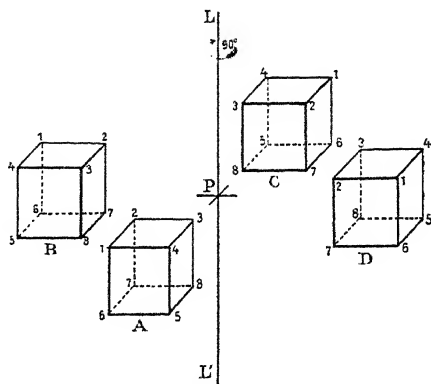


Fig. 6.

$A$ , by merely shifting them parallel to themselves along the plane of revolution. Thus, by definition, the rotations through angles of  $90^\circ$ ,  $2 \times 90^\circ$ ,  $3 \times 90^\circ$  round an axis parallel to one of the edges of the cube, are *characteristic* rotations for the symmetry of this figure. As the positions  $B$ ,  $C$ , and  $D$  differ from  $A$ , these three characteristic rotations are *non-equivalent*. A rotation through an angle of  $360^\circ$  however would be equivalent to that through  $90^\circ$ , etc.

In the same way we should find, that if through some point in space  $Q$  a straight line were drawn parallel to one of the four longest diagonals of the cube, rotations through angles of  $120^\circ$  and  $2 \times 120^\circ$  round this line as an axis, would appear to be "characteristic motions" too. It is easily seen that for the plane drawing of *fig. 3*, rotations through  $72^\circ$ ,  $2 \times 72^\circ$ ,  $3 \times 72^\circ$ , and  $4 \times 72^\circ$  round an arbitrary axis passing through a point  $R$  in space and perpendicular to the plane of the drawing, are also characteristic motions, and non-equivalent ones.

In the same way it must be evident that if the rotation of the cube  $A$  in *fig. 6* around  $LL'$  had been through an angle differing from those mentioned, coincidence could not have been realised by shifting alone; and the same would have been the case, if the rotations around  $LL'$  through  $90^\circ$ , etc., were applied to a different figure instead of to a cube, e. g. to an unsymmetrical figure.

*Characteristic motions for a symmetrical figure therefore are in general those by which the figure is brought into positions parallel to the initial one, but yet differing from it.*

It is of importance to point out here, that the translations mentioned are reduced to zero, when the point  $P$  in space is so chosen, that

it coincides with the „geometrical centre”  $O$  of the

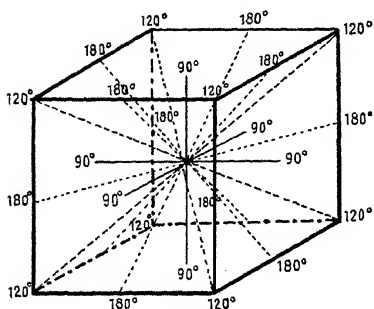


Fig. 7.

rotation it will now occupy the same place in space, although of course always with interchanged corners, etc., — just in the same way as happened in the rotations first considered.

The symmetry of a stereometrical figure may

now be exactly defined as *the total complex of its non-equivalent characteristic motions*, as long as only symmetry-properties of the kind here considered are dealt with.

§ 2. The second case that we must now consider in detail is, when a figure  $F$  in a position  $S_1$  is reflected in a mirror. It is then transformed into its mirror-image  $F'$  and brought into a new position  $S_2$ ;  $F'$  is of course now no longer congruent with  $F$ . Accordingly, the manipulation required to make them coincide is no longer a simple motion, some further operation being required besides it.

If a symmetrical figure is of such a kind that it is equal to its mirror-image in several ways, then it will be always possible to find for that figure a series of *characteristic reflections*, in the same sense as we have spoken of characteristic motions. In this case too the point  $P$  in space, through which the mirror-planes are drawn, may be chosen in such a way that the translations by which the reflected figures are finally shifted to the place of the original one, are reduced to zero; the figure  $F$  then remaining in the same place, but in different positions after each reflection. In the case of the cube,  $P$  had to be made to coincide with the centre  $O$  already mentioned, the nine ( $3 + 6$ ) possible characteristic reflecting planes all passing through  $O$ .

As we shall soon see, a figure being in several ways equal to its

mirror-image, will however have not only "characteristic reflections" but these will be necessarily accompanied by some "characteristic motions" also.

*Thus in general we can maintain that the symmetry of a stereometrical figure is known exactly, when the whole complex of its non-equivalent characteristic motions and reflections is determined.*

§ 3. More detailed investigation shows that reflection in a

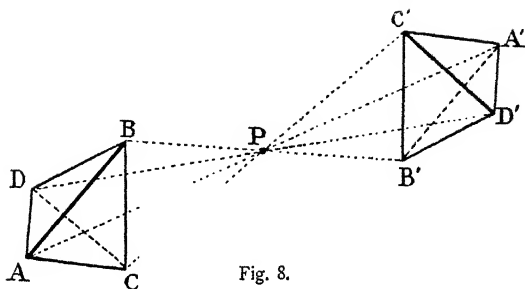


Fig. 8.

mirror-plane is not the only way, in which a figure  $F$  can be transformed into its mirror-image. In *fig. 8*  $ABCD$  is an arbitrary, irregular tetrahedron. If now a point  $P$  in space be chosen, and straight lines be drawn through  $P$  from every point of  $ABCD$ , and each respectively continued to an equal length beyond  $P$ , a number of points will be found, which joined together form a similar tetrahedron  $A'B'C'D'$ . This tetrahedron however is *not* congruent with  $ABCD$ , but is its *mirror-image*; we say that it is obtained from  $ABCD$  by *inversion* with respect to the point  $P$ , this point being called the *centre of inversion*. However it can be easily proved, that the transition of  $ABCD$  to  $A'B'C'D'$  could have taken place also in the following way: suppose  $ABCD$  to be first rotated through an angle of  $180^\circ$  round an arbitrarily chosen axis  $LL'$ , passing through  $P$ , and then the tetrahedron in this new position to be reflected in a plane perpen-

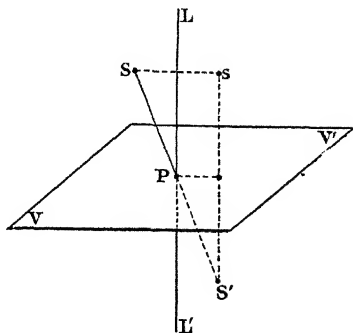


Fig. 9.

pendicular to the plane of rotation. This method shows that the transition from a figure to its mirror-image can be achieved through a combination of rotation and reflection, rather than just inversion through a point.



pendicular to this axis  $LL'$ , and meeting it at  $P$ . From *fig. 9* it will be seen at once, that a point  $S$  in the figure  $F$ , by the rotation through  $180^\circ$  round any axis  $LL'$  through  $P$ , will arrive at  $s$ , and by a further reflection in the plane perpendicular to  $LL'$  will be brought to  $S'$ . The transformation of  $S$  into  $S'$  is however evidently equivalent to an inversion with respect to  $P$ , and it can easily be seen that the result is quite independent, as well from the special choice of  $LL'$ , as from the sequence of reflection and rotation, so long as the reflecting plane  $VV'$  be only kept perpendicular to the axis  $LL'$ .

**§ 4.** *From this it will be easily understood that every transformation of a figure  $F$  from a definite original position  $S_1$  into its mirror-image  $F'$  with a position  $S_2'$ , can always be executed by a combination of some rotation round an axis  $LL'$  and a successive reflection in a plane  $V$  perpendicular to that axis.*

For by the inversion of  $F$  with respect to an arbitrarily chosen point in space  $P$ , it moves from the position  $S_1$  into a position  $S_1'$ , in which it is changed simultaneously into its mirror-image  $F'$ . Since the figure in this new position  $S_1'$ , and that in the desired final position  $S_2'$  now are *congruent*, (for they are both mirror-images of the same figure  $F$ ) the transition of  $S_1'$  to  $S_2'$  can be made by a single rotation through an angle  $\alpha$  round an axis  $LL'$  passing through  $P$ , — if only the point  $P$  be suitably chosen, so as to coincide with the geometrical centre of  $F$ : otherwise a translation must finally also be made to complete the transition of  $S_1'$  into  $S_2'$ .

This however does not affect the general validity of the demonstration. Now the inversion can be substituted by a rotation through  $180^\circ$  round an axis which for this purpose can be made coincident with the above mentioned axis  $LL'$ , — the whole angle of rotation now becoming  $(\alpha + \pi)$ , and a reflection in a plane  $V$  perpendicular to  $LL'$ . The total transition from  $S_1$  to  $S_2'$  is thus performed by a single rotation through an angle  $(\alpha + \pi)$  round an axis  $LL'$ , and a reflection combined with it, in a plane  $V$  perpendicular to this axis  $LL'$ .

Another demonstration of this important theorem will be given at the end of this chapter as a consequence of our considerations of repeated reflections in several planes.

**§ 5.** A few remarks must now be made on the difference of *finite* (limited) and *infinite* (unlimited) figures in general. Instances of such *finite* figures are polyhedra, and all objects with a limited form.

On the other hand unlimited systems of points distributed in space, as considered for instance in the theories of molecular structures, etc., are examples of *infinite* systems.

We will suppose such an infinite system to be under investigation, and let the most general type of motion, the *helicoidal* one, be in some way characteristic of it. If this helicoidal motion is executed, *no* point whatever of the system will appear to remain in space in its original position, in consequence of the *translation*, which is included in every helicoidal motion<sup>1)</sup>; however the figure as a whole, remains *at the same place in space*. This is expressed also by saying that to every point of an infinite system an infinite number of homologous points of the system always correspond. If a *finite* system be subjected to a helicoidal motion, the rotation of which corresponds to one characteristic of the figure under investigation, it will reach a position such that a single translation would bring it back to its original place; by the motion considered, the figure comes into a new place in space, making it coincide with the figure itself. In the infinite system an infinite number of homologous points correspond to every point; in the finite figure only a limited number. In the infinite system the translations mentioned have thus a real importance with respect to the special character of the unlimited symmetrical arrangement; in the finite figure, however, those translations evidently are of no interest, as long as the particular symmetry of the limited figure (polyhedron e. g.) is regarded as being defined by its characteristic motions or reflections. From this we can safely conclude, that helicoidal motions can have no significance as characteristic motions for finite systems; only those need be considered here, the translations of which are equal to *zero*, i. e., when they are simple *rotations* about an axis.

Thus for the description of the symmetry of *finite* figures, the translation, and the helicoidal motion also, may from the first be excluded as characteristic motions. For the definition of the special symmetry-character of such figures it thus appears to be sufficient to suppose only one point *O* of the figure, — the geometrical centre mentioned previously, — to remain fixed in space during all symmetrical operations to which the figure may be subjected. As already said, it is always possible to choose this point *O* so

1) Vid: A. K. Boldyrew, Verh. der Kais. russ. Miner. Ges. St. Petersburg, (2). 45. (1907), Def. 7 and its Coroll. 8.

that the whole figure remains in its original place in space during all motions and reflections which are characteristic of its symmetry.

It may here be emphasized once more, that among the number of their characteristic motions, *infinite* symmetrical figures always possess *translations* too, and such figures *can* therefore eventually have helicoidal motions also. For several of such systems, especially for those which play an important rôle in the theories of crystalline structure, such helicoidal motions are really typical.

§ 6. For the time being we can leave the discrimination between the two cases of finite and infinite figures, and proceed with our task of characterising the various typical operations for the determination of their possible symmetries.

An arbitrary stereometrical figure, of which one point  $O$  remains fixed in space, can always be brought from a position  $S_1$  into another position  $S_2$ , where-in it is congruent with itself, by a single and completely determined rotation round an axis  $A$ , passing through the fixed point  $O$ . This is the well-known theorem of Euler<sup>2)</sup>, by which all rotatory motion in elementary mechanics can be treated in a very simple way.

It follows from this, that the most general characteristic motion of a *finite* symmetrical figure which is congruent with itself in several

<sup>1)</sup> The theorem of Euler can easily be proved, as soon as the validity of the thesis is accepted that *two rotations round two axes  $A$  and  $B$  intersecting in  $O$ , are together always equivalent to a third rotation round an axis  $C$ , passing through  $O$  also*. The demonstration of this is given later on. Now, if the validity of this theorem be accepted, we can demonstrate the theorem of Euler easily. For let the figure  $F$  now be brought from its original position  $S_1$  into a final position  $S_2$ , a point of it  $O$  remaining fixed in space. One of the straight lines of  $F$ , e.g.  $OL_1$  may be brought into its new position  $OL_2$  by the said transition. We imagine a plane passing through  $OL_1$  and  $OL_2$ , and consider the normal  $N$  there-on in  $O$ ; the directions  $OL_1$  and  $OL_2$  may include an angle  $\alpha$ ; If now the figure  $F$  be rotated round  $N$  over an angle  $\alpha$ ,  $OL_1$  comes into  $OL_2$ , and the new position of  $F$  is  $S_1''$ . To bring it from  $S_1''$  to  $S_2$ , we have only to rotate it round  $OL_2$ ; for  $OL_2$  has in  $S_2$  the same position as it has now, its points thus remaining fixed in space, and those therefore being points situated on a true „axis” of rotation.

The whole transition from  $S_1$  to  $S_2$  therefore can be considered to be equivalent to the rotations round  $N$  and  $OL_2$ , and these are equivalent to a rotation round some axis  $C$ . The problem to find this third axis  $C$ , if the positions of two others are given, will be gone into at the end of this chapter, after the general method of reasoning by means of repeated reflections has been described.

ways, is only *the rotation round an axis*. We shall define such figures as these, as possessing only *symmetry-properties of the first order*: the characteristic motions are rotations through definite angles  $\alpha$ , and round definite axes, and will be known as *axes of symmetry of the first order*. These axes of symmetry are therefore named the *special symmetry-elements of the first order*.

If however the figure is of such a nature, that it is equivalent to its mirror-image in several ways, and if here too the point  $O$  is supposed to remain fixed in space, we have seen already that besides the symmetry-properties of the first order, there must also be introduced other symmetry-properties by which the figure is changed into its mirror-image. It is then said to possess *symmetry-properties of the second order* too; and as already has been demonstrated, the characteristic operation corresponding to these, will generally consist in definite rotations about a certain axis, inseparably combined with a constantly repeated reflection in a plane perpendicular to that axis.<sup>1)</sup> This remarkable species of axis will be discriminated by us in the following pages as an *axis of symmetry of the second order*, or a *mirror-axis*. The mirror-axis is the characteristic *symmetry-element of the second order*, just in the same way as the ordinary symmetry-axis is for symmetrical figures of the first order.

If in fig. 10  $\bar{A}_4$  is a mirror-axis with the characteristic angles of rotation  $90^\circ$ ,  $180^\circ$ ,  $270^\circ$ ; the arrow will give the positions indicated, if subjected to the four characteristic operations essential for the axis  $\bar{A}_4$ . It is obvious that the *inversion* and the ordinary *reflection* in a mirror-plane are *only special cases of the mirror-axis*: for  $\alpha = 0^\circ$ , we have the *pure reflection*; and for  $\alpha = 180^\circ$ , as was demonstrated above, we have the *inversion*.

§ 7. In a well-known theorem of elementary mechanics, which is also named after Euler, it is proved that if two rotations around two intersecting axes are executed successively, they are together equivalent to a rotation round a third axis, passing through the point of intersection.<sup>2)</sup>

From this it follows, that if a symmetrical figure possesses two

1) The rotation about the axis and the reflection in a plane perpendicular to it have no significance here independent of each other: only the *result* of their *combined* action must be taken into account.

2) A simple demonstration is given at the end of this chapter, as a corollary of a general theorem by BOLDREW.

characteristic rotations round the axes of symmetry  $A$  and  $B$ , intersecting in the fixed point  $O$  of the figure, this last must necessarily

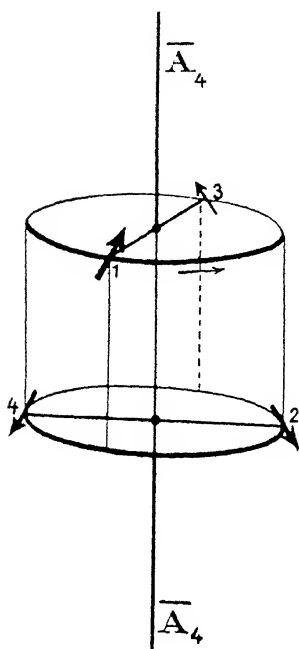


Fig. 10.

have a third characteristic rotation round another symmetry-axis passing through  $O$ . The last rotation is equivalent to the former two, executed in succession. Thus from the existence of *two* axes of symmetry the existence of a *third* necessarily follows.

But if the figure considered has two axes of the *second* order, intersecting in  $O$ , the resulting manipulation must be an ordinary *rotation* about an axis of symmetry of the *first* order, passing through  $O$ . For by the first operation of the second-order the figure  $F$  is transformed into its mirror-image  $F'$ , and this is in its turn changed by the operations corresponding to the second mirror-axis into a figure *congruent* with the initial one. Executed successively they are therefore together equivalent to an ordinary rotation; and this is

evidently the same thing as the assertion made already (page 14 and 15), that a figure cannot possess several symmetry-properties of the second order *alone*, without the simultaneous possession of those of the first order too.

From both these examples it will be clearly understood that there are essential mathematical relations connecting the different symmetry-properties of one and the same figure *simultaneously* present. Thus the simultaneous existence of two such properties always requires the existence of a third one equivalent to the other two combined. It is precisely the existence of such relations, that makes the whole doctrine of symmetry a possibility, and permits us to deduce the general classes of symmetrical types by mere mathematical reasoning.

§ 8. However in this connection the question might rise: what

will happen, if those simultaneous axes of symmetry do not intersect, for instance if they cross in space?

Now it can be demonstrated <sup>1)</sup>, — and the method will be briefly shown later on, — that the operation resulting from the presence of two crossing axes of rotation must be a *helical* motion, with a translation differing from zero. In the same way it can be shown, that if a figure has two axes of symmetry of the second order, which do not intersect, the resulting motion will also be *helical*; etc. From these few examples it will be seen that such cases cannot occur in *finite* symmetrical figures, the helical motion there being excluded for reasons already given.

*In the case of finite symmetrical figures therefore, it is strictly necessary that all possible symmetry-elements of the first and of the second order should pass through the same fixed point O*; thus also the planes of reflection must eventually pass through it, and if an inversion centre be present, that must also coincide with this point *O*. It will be discriminated, as previously said, as the *geometrical centre* of the figure *F*; eventually it may play the rôle of an inversion-centre (centre of symmetry) also, but this *need not* be always the case.

However, *infinite* figures may certainly have symmetry-elements, *not* passing through one and the same point simultaneously. In such unlimited systems there may be present parallel, intersecting, and crossing axes of the first or of the second order, sets of parallel reflecting planes, etc.

In respect to the foregoing therefore it seems necessary also to consider the finite symmetrical systems apart from the infinite ones.

§ 9. In this connection it seems advisable to consider in some detail the general character of the axes of symmetry of the first and second order and to examine more in particular the results of repeated reflections in several planes, before the possible combinations of symmetry-elements are systematically discussed. For these investigations appear to be of great importance for the purpose of understanding the doctrine of symmetry in general, and for the demonstration of its theorems.

*a. Axes of symmetry of the first order.*

The axis of symmetry of the first order is in each case determined by its special direction in space, and by its own character which

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<sup>1)</sup> All these theorems are gone into thoroughly by A. K. Boldyrew, Verh. der Kais. russ. Miner. Ges. St. Petersburg, (2). 45. (1907); vid. theorems 29 till 38, and 25 till 28, and also the problems 7 till 11 in his paper.

is known when its *characteristic angle of rotation*  $\alpha$  is given. That angle is defined as the *smallest* angle, through which the symmetrical figure must be rotated round the axis considered, to make it coincide

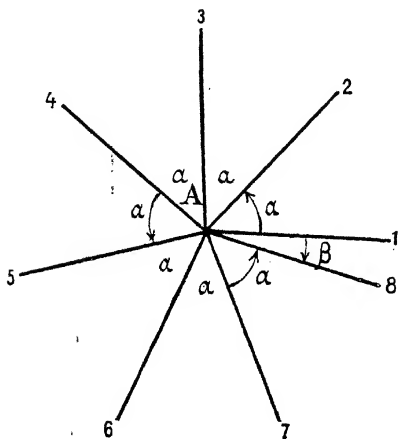


Fig. 11.

with itself. Of course the axis is supposed to pass through the geometrical centre of the figure  $O$ .

If this angle is  $\alpha$ , the figure will also be brought to self-coincidence by rotations through  $2\alpha, 3\alpha, \dots, n\alpha$ , the number  $n$  being an integer part of  $2\pi/\alpha$ . For if this were not the case (fig. 11), then, after  $n$  times turning round the axis  $A$ , a straight line of the figure

figure  $AL_1$  situated in a plane perpendicular to  $A$ , would finally reach the position  $AL_n$  and because the figure is still congruent with itself,  $AL_1$  could be brought into the position  $AL_n$  by turning the figure round  $A$  in an opposite direction over the angle  $\beta$ , this being smaller than  $\alpha$ . It then follows that  $\beta$  would also be a *characteristic* angle of the figure when rotated round its axis of symmetry  $A$ , which is impossible, because  $\alpha$  is supposed to be the *smallest* angle of this kind. Obviously  $\beta$  must thus be equal to zero, and therefore:

$$\alpha = \frac{2\pi}{n}, \text{ where } n = 1, 2, 3, 4, 5, \dots \text{ etc. to } \infty.$$

The number  $n$  determines the *period* of the axis  $A$ , and can have all integer values between 1 and  $\infty$ , for  $n = \infty$ ,  $\alpha$  being 0. The axes are, according to the values of  $n$ , regarded as *binary* ( $n = 2$ ) *ternary*, *quaternary*, *quinary*, *senary*, etc. axes.<sup>1)</sup> For  $n = \infty$ , the axis is called an *axis of isotropy*, and it has a special importance with respect to many *physical* phenomena, as we shall see afterwards.

<sup>1)</sup> They are also called axes of *threefold*, *fourfold*, etc. symmetry, or *trigonal*, *tetragonal* etc. axes. These last names are however exclusively usual in crystallography.

*b. Axes of the second order.*

In the same way we may distinguish the axes of the second order with respect to their particular period. However it must be distinctly remarked, how a closer examination will soon prove that in many (*not in all*) cases, axes of the second order can be replaced by those of the first order, if combined with a real reflecting plane or with a centre of inversion. It is therefore our task to investigate

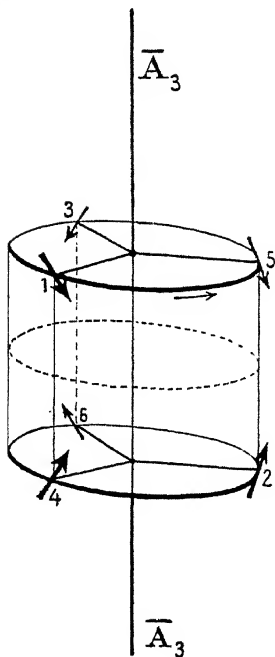


Fig. 12.

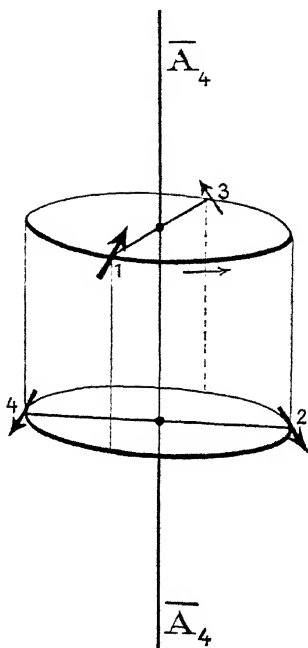


Fig. 13.

when this is possible and when not. Already two cases of this kind have been dealt with: the binary axis of the second order ( $n = 2$ ) was equivalent to the inversion, and in the case, where  $n = 1$ , the axis was equivalent to the reflection in a real plane. The first value of  $n$  to be examined is thus  $n = 3$ . Let  $\overline{A}_3$  be a ternary axis of the second order (*fig. 12*) and let us consider, which positions the arrow 1 will successively reach. Let us execute all rotations round  $\overline{A}_3$ , and combine them with the reflections inseparably connected



with them, because  $\overline{A}_3$  is an axis of the *second* order. Then we shall find the arrow repeated six times in such positions in space, that the complete set of the six arrows thus obtained has a symmetry which can also be described by the presence of a ternary axis of the *first* order and a real reflecting plane perpendicular to it. This can easily be seen from a figure or a suitable model.

If  $n = 4$  however, we shall find in the same way, that the complete

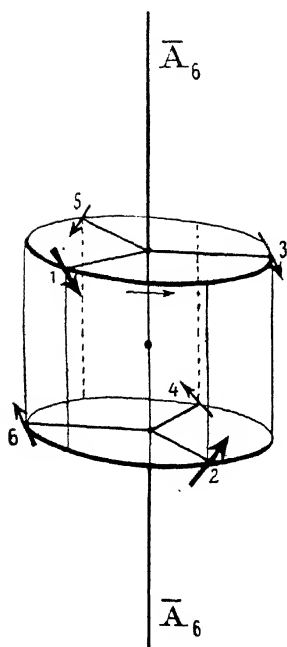


Fig. 14.

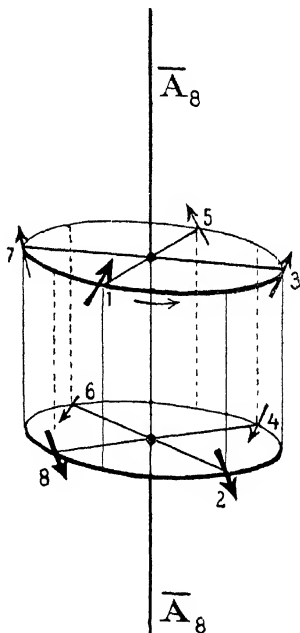


Fig. 15.

set of different positions reached by the arrow is that represented in the *fig. 13*. Although  $\overline{A}_4$  appears to be also an axis  $A_4$  of the first order with a period  $\frac{2\pi}{4}$ , it is evidently *not* possible now to substitute  $\overline{A}_4$  by other symmetry-elements which can completely describe the particular symmetry of the figure thus obtained.

For  $n = 5$  we shall find, on examination, that the axis of the second order  $\overline{A}_5$  is also an axis  $A_5$  of the first order, combined with a plane of symmetry perpendicular to it. This case is thus evidently wholly

analogous to that of the ternary axis of the second order dealt with in the above.

For  $n = 6$ , an analogous reasoning (*fig. 14*) shows, that this axis is equivalent to a *ternary* axis of the first order, combined with an *inversion*. Indeed, the arrow will successively reach the positions 1, 3, and 5, and 2, 4, and 6, so that e.g. 4 could also be obtained from 1, 5 from 2, 6 from 3, etc., by simple inversion with respect to a centre of symmetry  $O$ . For  $n = 7$  the result would have been analogous to the case of  $n = 3$ , or  $n = 5$ ; for  $n = 8$  however, we should have found an arrangement of the arrows, such as is represented in *fig. 15*, and here again it appears that the complete symmetry of the set of arrows obtained, *cannot* be described by another combination of symmetry-elements, just as is the case when  $n$  is equal to 4. Later on we shall consider these cases in a more general way. For the present it will be sufficient to formulate the results obtained as follows here:

An axis of the *second* order with a period of  $\frac{2\pi}{n}$ , is equivalent to an axis of the *first* order of the *same* period, combined with a *real reflecting plane perpendicular to it*, if  $n$  is an *odd* number.

If however  $n$  is an *even* number, two cases must be considered: 1) if  $n$  be divisible by 4: in this case the axis of the second order *can never* be replaced by another combination of symmetry-elements. And 2) when  $n$  is *not* divisible by 4 ( $\frac{n}{2}$  thus being *odd*):

in this case the axis of the second order with a period of  $\frac{2\pi}{n}$  is equivalent to an axis of the first order with a period-number  $= \frac{n}{2}$ , combined with a *centre of symmetry*.<sup>1)</sup>

§ 10. These two symmetry-elements, the axis of the first and that of the second order, now having been considered in detail, it is of importance to notice here the result of *repeated reflections* in different mirror-planes, simultaneously present. It is supposed in this and all following cases, that the reflecting planes *do not act*

1) From this it appears, that the centre of symmetry and the plane of reflection are *not* sufficient to deduce all possible symmetries of those groups which only have axes of the first order. As soon as an axis has a period whose number  $n$  is divisible by 4, the addition of a centre or of a plane of symmetry can *not* lead to an exhaustive treatment of all possible kinds of symmetry. Indeed, on account of this, Bravais omitted in his famous deduction of the possible groups of symmetry, the corresponding group of symmetrical polyhedra.

independently of each other, but that only the result of their *combined* action is always considered.

The case of a single reflecting plane has already been dealt with, and its general character is now assumed to be understood.

We will therefore proceed to the case when *two* planes of symmetry

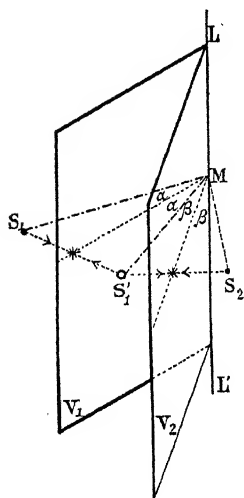


Fig. 16.

intersect in a line  $LL'$  (fig. 16). A point of the figure  $P$  is reflected in  $V_1$ , and its mirror-image is  $P'$ ; then  $P'$  is reflected in  $V_2$ , and arrives in  $P_2$ . The figure  $F$  after these two consecutive reflections will be congruent with itself, and therefore the final position could also be obtained from the initial one by *rotating* every point of it  $P$  through a characteristic angle  $2\alpha$  round  $LL'$ , the axis of intersection of the two reflecting planes, containing between them an angle, the value of which is  $\alpha$ . The repeated reflection in two planes intersecting under an angle  $\alpha$ , thus appears to be equivalent to a rotation about the line of intersection through an angle  $2\alpha$ .

Of course it is clear, and it can easily be demonstrated too, that every rotation

about an axis  $LL'$  through an angle  $\alpha$  may be replaced by two successive reflections in two mirror-planes, intersecting along  $LL'$  under an angle  $= \frac{\alpha}{2}$ .

If both mirrors are *simultaneously* turned around  $LL'$  over an angle  $\beta$ , while keeping the enclosed angle between them unaltered ( $= \alpha$ ),  $P_1$  will reach the same final position  $P_2$ , and the same is true for every point of the figure  $P$ . Of course the succession of both the reflections considered must remain the same as before.

The change of position of  $F$  thus appears to be quite independent of such a simultaneous motion of both mirror-planes.

This is a very important principle, and it can be used, as e. g. Boldyrew<sup>1)</sup> showed in many cases, for the demonstration of a number of very interesting theorems in the doctrine of symmetry. A special case is that in which the angle  $\alpha$  is infinitely small, the inter-

<sup>1)</sup> Boldyrew, *loco cit.*

section  $LL'$  thus being situated at an infinite distance. The two planes  $V_1$  and  $V_2$  (fig. 17) are then parallel; their distance apart may be  $a$ . The repeated reflection is now evidently equivalent to a *translation*  $= 2a$ .

Such translations and parallel planes of reflection are often characteristic of *infinite* figures or systems; for *finite* figures they have *no* importance. It is moreover evident that in the last mentioned case the result will remain unaltered, if both planes are shifted parallel to themselves, provided that their mutual distance be kept constant  $= a$ .

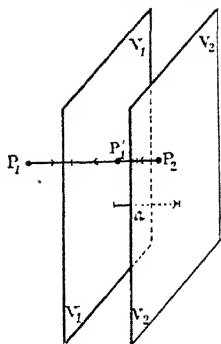


Fig. 17.

§ 11. Now we shall consider the case when reflection occurs successively at *four* reflecting planes which do not act independently of each other, and which pass through the same point  $O$ . Then it can be easily proved by the aid of the principle of the simultaneous rotation of two intersecting planes just mentioned, that these successive reflections in four planes are equivalent to a reflection in *two* planes passing through  $O$ ; or, which is the same thing, to a single rotation around an axis passing through  $O$ .

Let the four planes considered be  $S_1$ ,  $S_2$ ,  $S_3$ , and  $S_4$ ;  $S_1$  and  $S_2$  may intersect along a straight line  $OL_{1,2}$ , and  $S_3$  and  $S_4$  along  $OL_{3,4}$ .

Now we can first turn the two mirror-planes  $S_1$  and  $S_2$  simultaneously round  $OL_{1,2}$ , until  $S_2$  passes through  $OL_{3,4}$ ; the effect of the successive reflections in  $S_1$  and  $S_2$  will *not* be altered by this, provided that the angle of intersection  $\alpha$  between  $S_1$  and  $S_2$  remain the same. Now we will turn the planes  $S_3$  and  $S_4$  together round their intersection  $OL_{3,4}$ , until  $S_3$  passes through  $OL_{1,2}$ . There will be no change in the effect of the successive reflections in  $S_3$  and  $S_4$  by this. But now  $S_2$ , as well as  $S_3$ , coincides with the plane passing through  $OL_{1,2}$ ; and  $S_1$  and  $S_4$ , the reflections in the planes  $S'_2$  and  $S'_3$ , — being the new positions of  $S_2$  and  $S_3$ , — neutralising each other. Thus there remain only the successive reflections in two planes  $S'_1$  and  $S'_4$ , these being the positions of  $S_1$  and  $S_4$  finally reached after completing the above mentioned turnings of the four original planes. The reflections in  $S'_1$  and  $S'_4$  are together equivalent to a rotation round their intersection through a certain

angle, this axis of course also passing through  $O$ . The figure  $F$  remains obviously congruent with itself in these successive operations because their number is even.

It will be immediately clear from this that the theorem of Euler previously mentioned can now be demonstrated without the slightest difficulty. For in this theorem it was stated that the successive rotations over angles  $\alpha$  and  $\beta$  round two axes  $A$  and  $B$ , intersecting in  $O$ , are always equivalent to a rotation over a certain angle  $\gamma$  round a third axis  $C$ , also passing through  $O$ . Now for every rotation of both  $A$  and  $B$ , there may be substituted a successive reflection in two mirror-planes passing through  $A$  and  $B$ , and intersecting at angles  $\frac{\alpha}{2}$  and  $\frac{\beta}{2}$  respectively. But then we have the above mentioned case of four planes intersecting in a single point  $O$ . Thus the result is equal to a single rotation round  $C$ , also passing through  $O$ , through a definite angle  $\gamma$  which can be easily found by geometrical construction from the angles  $\alpha$  and  $\beta$ <sup>1</sup>). This fundamental theorem is now sufficiently demonstrated, and the base is established for the mathematical treatment of the symmetry-problem in those cases in which only *axial* symmetry is considered.

If the four planes do *not* pass through the same point  $O$ , an additional *translation* will happen to add to the resulting rotation, a *helicoidal* motion thus being substituted for the single final rotation mentioned above. But in this case also the general conclusions will still be valid, it being only necessary (for *infinite* figures) to substitute the helicoidal for the ordinary rotation. Of course in this case too, the figure remains congruent to itself.

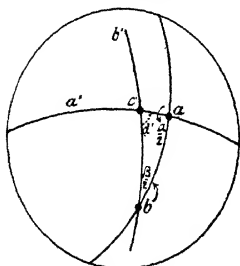


Fig. 18.

Take  $O$  as centre of a sphere (fig. 18),  $a$  being the point of intersection of its surface with  $A$ ,  $b$  being the same for  $B$ . Let  $ab$  be joined by a great circle. Now if the great circle  $aa'$  be so constructed, that the angle  $a'ab$  is  $\frac{\alpha}{2}$ , and in a sense *opposite* to the direction of the rotation round  $A$ ; and if  $bb'$  be a great circle, constructed in the *true* sense of the rotation round  $B$ ,  $b'ba$  being equal to  $\frac{\beta}{2}$ , the intersection  $c$  is the point, where the new axis  $OC$  pierces the surface of the sphere, and its characteristic angle is equal to  $2\delta = \gamma$ , the sense of rotation being readily found.

§ 12. We can now put the question: what will be the final result of the successive reflections of a figure *in three arbitrarily situated mirror-planes*? Here also only the result of their *combined* action is investigated. Let the three planes be  $S_1$ ,  $S_2$  and  $S_3$ . We will now turn the planes  $S_1$  and  $S_2$  together around their line of intersection simultaneously, in the way mentioned before, until  $S_2$  passes through  $Z$ , being a *perpendicular* to  $S_3$ . The successive reflections at  $S_1$ ,  $S_2$ , and  $S_3$ , are now substituted by their equivalents in  $S'_1$ ,  $S'_2$ , and  $S_3$ , —  $S'_2$  being thus perpendicular to  $S_3$ . Now in the same way we can turn the planes  $S'_2$  and  $S_3$  simultaneously round their intersection (their enclosed angle ( $= 90^\circ$ ) of course being kept unaltered), until at last  $S_3$  passes through the perpendicular to  $S'_1$ . The whole series of original reflections in  $S_1$ ,  $S_2$ , and  $S_3$ , is thus substituted by such in  $S'_1$ ,  $S''_2$ , and  $S'_3$ , of which  $S'_3$  is perpendicular to  $S'_1$ , as well as to  $S''_2$ .

But the reflections at  $S_1$  and  $S''_2$  being both perpendicular to  $S'_3$ , can be substituted by a rotation around their line of intersection  $L$ , this of course being a perpendicular to  $S'_3$ . The whole series of operations thus appears to be equivalent to a rotation around an axis  $L$ , combined with a reflection in a plane  $S'_3$  perpendicular to it; of course the figure  $F$  is transformed by this into its mirror-image  $F'$ .

We can therefore say in general<sup>1)</sup>: *The result of the successive reflections of a figure  $F$  in three arbitrarily situated planes not acting independently of each other, is equivalent to a certain rotation round an axis, combined with a reflection in a plane perpendicular to that axis, their point of intersection being the common point of the three planes. The figure  $F$  is changed thereby into its mirror-image  $F'$ .*

This resulting operation is evidently equivalent to what we have previously called a rotation round an *axis of the second order*.

§ 13. It will be easily seen that the successive reflections at  $n$  planes can be always reduced to one of the two proceeding cases, according as  $n$  is an *even* or an *odd* number. For if  $n$  is *odd*, it may be reduced to the reflections in *three* planes; and if  $n$  is *even*, to such in *four* planes. If  $n$  is *odd*, the figure  $F$  is finally changed into its mirror-image  $F'$ , while if  $n$  is *even*,  $F$  always remains congruent with itself at the end. The reduction to the two cases described in the above, takes place by turning every *two* new planes simultaneously,

<sup>1)</sup> C. Viola, Zeits. f. Kryst. **26**. 519. (1895).

until they pass through the point of intersection of the first three planes; etc.

In considering this, the truth of our previous statement is evident, that *the general characteristic symmetrical operation of the first order is the rotation round an ordinary axis or round a screw-axis, and that of the second order is the rotation round a mirror-axis.* (p. 19).

§ 14. From these deductions it will now be clear that all theorems concerning motions in space, as described by translations, rotations, and helicoidal motions, may be reduced to a combination of successive reflections in two, three, or four *not independently* acting, and therefore *partially virtual* mirror-planes. And by the principle of simultaneously turning every pair of intersecting mirror-planes, with their angle of intersection kept unaltered, through an arbitrary angle round their line of intersection, we can find without much trouble the resulting motion of a stereometrical system, if the composing operations are given.

Indeed, all theorems of the doctrine of symmetry may therefore be exactly demonstrated in this way, as was indicated by Boldyrew in the paper already referred to. Of this property, that a figure arbitrarily situated in space can always be made to coincide completely with a figure congruent with the first by a certain combination of successive reflections *in no more than three* mirror-planes which do not act independently from each-other, nor pass through the same straight line, C. Viola<sup>1)</sup> and G. Wulff<sup>2)</sup> have made use to give a systematical deduction of the 32 possible crystal-classes. The rotation round an axis of the first order is in this case always the result of successive reflections in two existent or virtual<sup>3)</sup> intersecting mirror-planes; the rotation round an axis of the second order is described as the action of three successive reflections in planes passing through one point *O*, and of which one is perpendicular to both the others. We can express this result by saying that all finite, symmetrical figures may be considered as being "caeleidoscope"-figures. However from the teacher's point of view, the method proposed by Viola and Wulff, elegant as it is, has some disadvantages in so far, that in such figures as differ from their mirror-images, such reflections can only have a *virtual* significance, these figures of course possessing *no* real planes of symmetry whatever.<sup>3)</sup>

1) C. Viola, Neues Jahrbuchf. Miner. Geol., und Pal., Beil. Band 10. 507. (1896).

2) G. Wulff, Zeits. f. Kryst. u. Miner. 27. 556. (1896).

3) Indeed "virtual" planes of reflection, as they are *not* acting independently

This fact may cause some confusion, especially to students to whom these reasonings are new.

But as a mere mathematical method, the conception mentioned may be of general use; and it is of importance to recognise this fact, in case some special theorems relating to the general symmetry of stereometrical figures have to be strictly demonstrated.

In the next chapters we shall now proceed to the final deduction of all the possible combinations of symmetry-elements, and to a rational classification of them for the purpose of morphological description in general.

from each other, but only the "final effect" of their cooperation is considered here. Therefore in the case where an axis of the first order be replaced by two intersecting mirror-planes, including an angle  $\alpha$ , only *half the number* of points produced by the successive reflections must be taken into account; and where the axis of the second order is replaced by the cooperation of three mirrors, the third of which is perpendicular to both the others, only a *fourth* of the points produced by the reflections must be considered in these deductions. *Wulff* therefore distinguishes the action of such combined mirrors as *hemi-*, resp. *tetarto-symmetry*. We shall call the mirror-planes *real* planes of symmetry, if *all* points produced in the successive reflections are taken into account; in all other cases the reflecting planes have only *virtual* significance for the symmetry of the figure considered.



## CHAPTER III.

*Equivalent and Non-equivalent Operations. Definition of Group. The Problem of the possible Classes of Symmetry as a Problem of the Theory of Groups. The Axial-Groups. Some general Theorems. Cyclic, Dihedral and Endospherical Groups. — Symmetry-Centre and Enantiomorphism.*

§ 1. In this and the next chapter it is proposed to investigate, what combinations of symmetry-properties are possible in the case of *finite* figures and objects, and in what way the various types of symmetrical figures can be classified. Attention was drawn in the previous chapter to the important fact that *not every* combination of symmetry-properties can exist, because the simultaneously existent symmetry-properties of a certain figure are always connected by special relations which allow of a mathematical treatment of the problem considered. With reference to the previous chapters, the reader will remember what has been said about the *equivalence* of symmetrical operations. In the same sense we shall speak in future of *equivalent* operations, as being those that bring a figure from its original position into *the same final position*. Thus e. g. if a regular hexagonal pyramid be rotated about its vertical axis through an angle of  $60^\circ$ , it will coincide with itself, because it now occupies the same part of space as before; but notwithstanding this, its new position is *different* from its initial one, and the same is the case if rotations around the same axis are executed through angles of  $120^\circ$ ,  $180^\circ$ ,  $240^\circ$ , and  $300^\circ$ . If rotated through  $360^\circ$ , the figure arrives however in *the same* position in which it was originally. All these rotations, except the last ones, therefore, are *non-equivalent* motions, quite independent of the fact that by each of them the pyramid will be brought to self-coincidence.

If a symmetrical figure possesses an axis of the first order with

a period:  $\alpha = \frac{2\pi}{n}$ , it possesses evidently  $n$  such non-equivalent rotations. For the whole series of rotations:  $A(x)$ ,  $A(2x)$ ,  $A(3x)$ , ...,  $A(nx)$  corresponds to a series of successive positions  $S_1, S_2, \dots, S_n$  which are all *different* from each other,  $S_n$  being finally identical with the initial position  $S_0$ .

Now these  $n$  non-equivalent rotations are connected with each other in a particular way. For if we take any *two* of them at random and if we perform these rotations successively, the result will be a third rotation which however appears *to be equivalent to one or other contained in the series of  $n$  terms*. Thus the combination of  $A(3x)$  and  $A[(n-5)x]$  e.g., will equal the rotations  $A[(n-2)x]$  or  $A[(n-8)x]$ , which are included in the series mentioned above; if we take  $A(6x)$  and  $A[(n-1)x]$ , the resulting rotations will be  $A[(n-7)x]$ , or  $A[(n+5)x]$ , i. e.  $= A(5x)$ , both of these being also included in the same series, etc. Looked at from this standpoint, we can say that this series of  $n$  non-equivalent rotations represents in a certain sense a *closed system of rotations*.

Such a closed system of quantities which are different from each other, but of which each two are together equivalent to some other term of the system, is called a *group of quantities*. The  $n$  non-equivalent rotations corresponding to an axis of symmetry with a period  $\alpha = \frac{2\pi}{n}$ , therefore, form an instance of this kind: they represent a *finite group of rotations*.

That the symmetry-properties of each figure now really represent a system of things forming a closed *group* of this kind, will be at once clear when the two facts mentioned in the last chapter, are remembered: viz: 1) that every two symmetry-properties of a figure when combined, always necessitate the existence of a third one, equivalent to them together; and 2) that the symmetry of a figure is absolutely known when all its non-equivalent symmetry-properties are known. *Finite* figures are characterised by a *limited* number of non-equivalent symmetry-properties; and the problem of finding all possible combinations of symmetry-properties of finite figures, is that of finding out *all finite groups of these properties*. The latter being determined by the corresponding rotations round axes of the first or of the second order, the problem to be solved can be described as that of determining all finite groups of rotations of the first and the second order.

§ 2. In this chapter we shall only deal with the relatively simple

cases in which the symmetry of the figures considered is characterised by the mere existence of axes of symmetry of the first order, i. e. by mere rotations. Such figures and objects therefore must always be *different from their mirror-images*; as we shall see later,

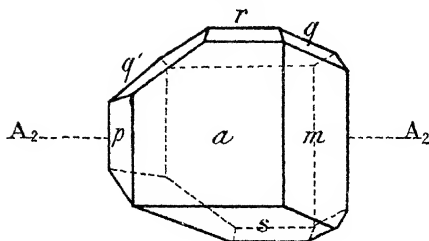


Fig. 19.  
*d*-Camphor-oxime.

$\frac{2\pi}{n}$  exists. The corresponding symmetry-groups contain  $n$  non-equivalent rotations, as mentioned before. We shall call them *cyclic groups*, and indicate them by the symbol  $C_n$ , where  $n$  may have any value from 1 to  $\infty$ .<sup>1)</sup>

As instances of symmetrical figures and objects of this kind, in fig. 19, 20, and 21, the crystal-forms of optically active *camphor-oxime*:  $C_{10}H_{16}NOH$ , of *sodium-periodate*:

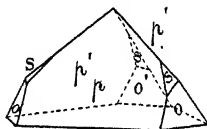


Fig. 20.  
*Sodium-periodate*.

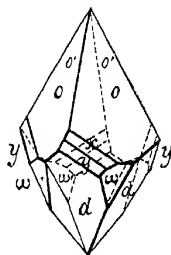


Fig. 21.  
*Wulfenite*.

$\gamma_4 + 3H_2O$ , and of *wulfenite*:  $PbMoO_4$  are

reproduced; the values of  $n$  are here 2, 3, and 4 respectively, and the axes are all placed vertically, with the exception of that of *camphor-oxime*, this being in horizontal position.

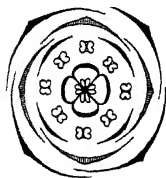


Fig. 22.  
Blossom-diagram of  
*Paris quadrifolia*.

Many parts of plants and animals possess this cyclic symmetry, as fig. 22 to 24 convincingly show, where the blossom-diagrams of *Paris quadrifolia* (fig. 22;  $C_4$ ),<sup>2)</sup> the fruits of *Chlamydia tenacissima* (fig. 23;  $C_3$ ) and of *Helic*

<sup>1)</sup> For  $n = \infty$  we have, properly speaking, no longer a *finite* group of rotations. This case will therefore be considered later on more in detail.

<sup>2)</sup> The *ternary* symmetry is generally found in *Monocotyledons*, and *Paris*

*teres baruensis* (fig. 24;  $C_2$ ) are reproduced, and in fig. 25 a part of a medusa: *Aurelia insulinda* (Haeckel), seen from below, and showing the symmetry of group  $C_4$ .



Fig. 23.  
Fruit of  
*Chlamydia tenacissima*.

As further instances the blossom-diagrams of *Triphasia trifoliata* ( $C_3$ ), of *Polemonium coeruleum* ( $C_3$ ), of *Hydrophyllum virginianum* ( $C_3$ ), and perhaps of *Roxburghia gloriosoides* ( $C_2$ ), might be mentioned.

If  $n = 1$ , the stereometrical figure has no symmetry at all; thus all asymmetric objects belong to this group  $C_1$ . As examples of natural objects of this kind, we may mention the blossoms of *Canna Sellowiana*, of *Valeriana*, of *Centranthus*, etc.; and some crystals, as e. g. *potassium-bichromate*:  $K_2Cr_2O_7$ , *strontium-hydrotartrate*:  $Sr(C_4H_5O_6)_2 +$



Fig. 24.  
Fruit of  
*Helicteres baruensis*.

$4 H_2O$ , *calcium-thiosulphate*:  $CaS_2O_3 + 6 H_2O$  (fig. 26).

§ 3. As to the special external aspect of all such symmetrical objects, we shall draw attention to the fact that in general one end of the symmetry-axis always shows a development of the symmetrically arranged parts, which is *different* from that at the other end of the axis. This phenomenon can, in accordance with the same phenomenon often observed in crystallography, be named *hemimorphy*.



Fig. 25.  
*Aurelia insulinda*.

*quadrifolia*, whose quaternary symmetry is present both in the blossom and in the phyllotaxis of the plant (Cf. J. Sachs, Vorles. über Pflanzen-physiologie, p. 600, Fig. 331), is a *rare* exception to this rule. On the other hand, the *five-fold* symmetry seems to be most general for *Dicotyledons*; sometimes also the *fourfold* symmetry appears to be of importance in this case.

Generally speaking, we can say that all objects possessing a cyclic symmetry  $C_n$ , have *hemimorphic* forms.

In *fig. 27* an imaginary fruit-form is represented, which may serve to give some impression of vegetable objects which perhaps may possess the symmetry of one of the groups  $C_n$ . (i. c. of  $C_6$ .<sup>1</sup>)

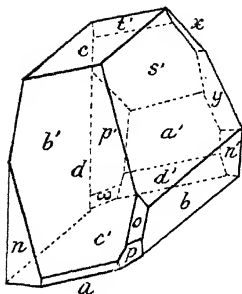


Fig. 26.

Calcium-thiosulphate ( $3H_2O$ ).

It is evident that all these objects must *differ from their mirror-images*; if the figures here reproduced, are reflected in a mirror, this fact will be grasped at once<sup>2</sup>). In many cases *only one* form of both possible is found in nature; why the other is not produced, can hardly be explained. With the problems relating to this, we shall deal more in detail later on.

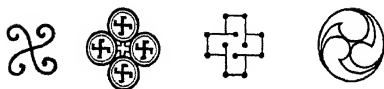
§ 4. II. We shall now proceed to the cases where several axes are simultaneously present, and begin with the simplest case of this kind, i. e. when *two binary axes*  $L_2$  and  $L'_2$  intersect in the geometrical centre  $O$  of the figure (*fig. 28*) at an angle  $\phi$ . In *fig. 28* the axes  $L_2$  and  $L'_2$  are supposed to be in the same plane as the drawing;  $ON$  may be the perpendicular to this plane in  $O$ . Because  $L_2$  is a binary axis ( $\alpha = 180^\circ$ ), a rotation round  $L_2$  will simply interchange both ends of the line  $ON$ , its lower and upper parts being reversed by it. If now a rotation round  $L'_2$  occurs through  $180^\circ$ , both ends of  $ON$  will interchange once more,  $ON$  therefore returning finally to its initial position. Thus  $ON$  must be itself



Fig. 27.

1) The symbols for these and the following groups are very convenient in morphology for the purpose of description. They are partly analogous to those of Schoenflies, partly analogous to those of P. Saurel, Zeits. f. Kryst. 50. 1. (1911).

2) It is a very remarkable fact that in several of the very ancient and universally used *religious symbols* of many peoples, this *axial* symmetry is also



distinctly and preferentially expressed. So in the so-called *fylfot*-symbols, mystic emblems of doubtful significance, of which an *Arabian*, *Hindu*, and *Scandinavian* form are reproduced here; and also in a *Japanese* symbol for "good luck". The symmetry indicated ( $C_4$  and  $C_3$ ) is easily recognisable in these widely spread symbols.

an axis of rotation, characteristic as a symmetry-element of the figure considered. Its typical angle of rotation  $\alpha$  can be easily found. For if  $OZ$  be a straight line of the figure situated in the plane  $(L_2, OL'_2)$ , this line will reach the position  $OZ'$  by the rotation round  $OL_2$ , and finally  $OZ''$  by the rotation round  $OL'_2$ ; it has thus come from  $OZ$  to  $OZ''$ , the angle  $ZOZ''$  being equal to  $2\phi$ . Since the same transition would occur if the figure were rotated round the axis of symmetry  $ON$  through its characteristic angle  $\alpha$ , this angle must be equal to  $2\phi$  also. We can therefore conclude from this:

*If a finite symmetrical figure possesses two binary axes including an angle  $\phi$ , it possesses also an axis of symmetry with the characteristic angle  $2\phi$ , perpendicular to the plane of the binary axes.*

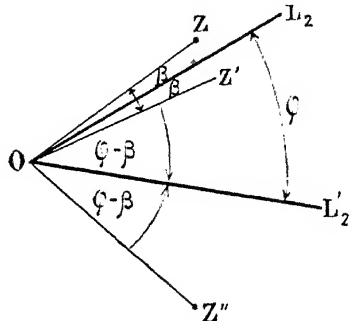


Fig. 28.

However, we can go yet farther. For it must be evident that if a figure  $F$  has a system of symmetry-axes, every characteristic

rotation round one of these axes must not only bring the figure  $F$  into coincidence with itself, but also the whole system of axes. If this were not the case, the group of symmetry-properties could not be a finite group. If now we make the characteristic rotations round  $ON$ , it is clear that we shall find in the plane  $(L_2OL'_2)$  several more binary axes, making with each other angles of  $2\phi$ ,

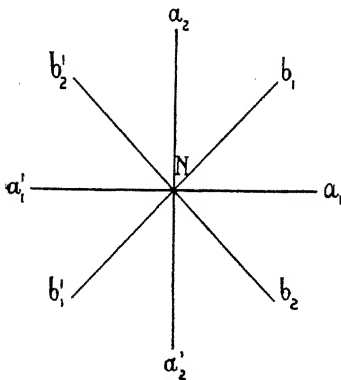


Fig. 29.

where  $2\phi = \frac{2\pi}{m}$ ,  $m$  being the

integer indicating the period of the axis  $ON$ .

In the same way we shall see that there are *two sets* of such binary

axes: one corresponding to  $OL_2$ , the other to  $OL'_2$ , the last axes being the bisectors of the angle between every two successive axes of the first set, etc. The truth of this can easily be seen from figure 29, where  $m = 4$ : by turning it round the perpendicular to the plane of the drawing  $N$ , it may be clear that only the

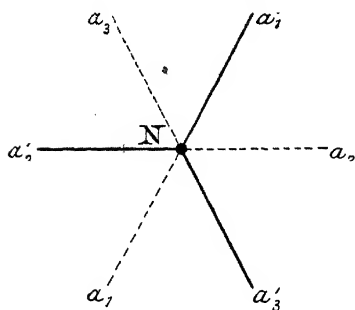


Fig. 30.

axes  $a_1Na'_1$  and  $a_2Na'_2$  will coincide, and in the same way  $b_1Nb'_1$  and  $b_2Nb'_2$ . Here, moreover, it appears that *both* ends of every axis will coincide with *both* ends of the other axis of the same set: thus e. g.  $Na_1$  with  $Na_2$ ,  $Na'_1$  with  $Na'_2$ , etc.

If however the number  $m$  characteristic for the axis perpendicular to the plane of the drawing, is not an even,

but an *odd* number, only one end of each axis will coincide with one end of each of the other ones: thus in *fig. 30*, where  $m = 3$ ,  $Na_1$  with  $Na_2$  and  $Na_3$ , but  $Na'_1$  only with  $Na'_2$  and  $Na'_3$  respectively. This is often expressed by saying that in the last case the binary axes are *heteropolar*, although they all belong to the *same* set, in contrast with the case first mentioned. There they were *homopolar*, however, the binary axes belong at the same time to two *different* sets.

The principal axis  $ON$  must of course be always *homopolar*, because binary axes perpendicular to it are present.

If we review the results obtained up till now in the cases considered, we can conclude therefore:

*There are groups of symmetry, characterised by a principal homopolar axis  $ON$ , with a period  $\frac{2\pi}{n}$ , —  $n$  being 2 or greater than 2, — and by  $n$  binary axes situated in a plane perpendicular to  $ON$  and intersecting at angles of  $\frac{\pi}{n}$ . These binary axes are homopolar, but belong alternately to two different sets if  $n$  is an even number; and the axes are equivalent but heteropolar if  $n$  is an odd number. The corresponding groups are named dihedron-groups, and they will in future generally be denoted by the symbol  $D_n$ .*

§ 5. With respect to these dihedron-groups  $D_n$ , it will be remembered that  $n$  can also have the value 2. In this special case we have to deal with figures which have *three* binary axes of three different kinds, and which are all perpendicular to each other. Figure 31 will make this clear; obviously every-one of the three axes will coincide only with itself if the symmetrical figure be subjected to its characteristic motions.

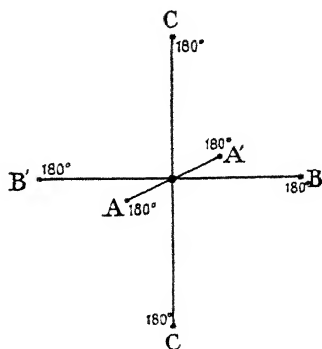


Fig. 31.

In fig. 32 and 33 two polyhedra with the symmetry of the groups  $D_3$  and  $D_6$  respectively, are reproduced as illustrations of figures of this kind. The binary axes are indicated, and it is easily seen from fig 32 and 33, that in the case of  $D_3$  both ends of these binary axes are in fact non-

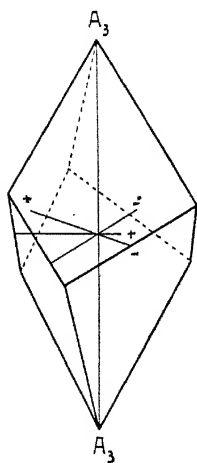


Fig. 32.

Trigonal trapezohedron.

equivalent, while in the case of  $D_6$  they are equivalent, but three of them have a function different from the three alternating ones. Moreover to every face  $Z$  there corresponds an equivalent face  $Z'$ , as a consequence of the existence of the binary axis, — both faces forming together a *dihedron*.

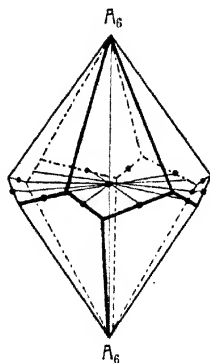


Fig. 33.

Hexagonal trapezohedron.

It is because of this peculiarity of the polyhedra of this kind, that the groups themselves got the name of dihedron-groups. Polyhedra of this symmetry are limited by irregular four-sided faces, and they are therefore commonly called *trapezohedra*. The figures 32 and 33 are instances of such *trigonal* and *hexagonal* trapezohedra;



but of course an infinite number of types of these polyhedra are possible,  $n$  having occasionally all values from 2 to  $\infty$ .

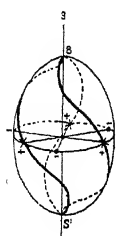


Fig. 34.

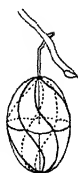


Fig. 35.

In nature there will perhaps be objects having the symmetry of the groups  $D_n$ . Up till now however the existence of no example of this kind has been proved with certainty; hence in *fig. 34* and *35* some imaginary "fruits" have been reproduced, in order to make clear what they would look like; the symmetry of them is  $D_3$  and  $D_6$  respectively. The principal difference from the case of the cyclic groups consists in the fact that the principal axis  $ON$  is *no longer heteropolar*, as was the case in the cyclic symmetry with its hemimorphic

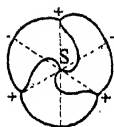


Fig. 36.

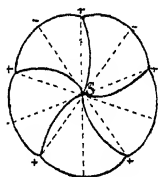


Fig.

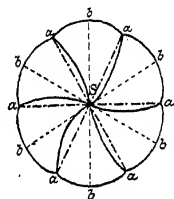


Fig. 38.

development of forms. Therefore this hemimorphic form is no longer observable here. In *fig. 36, 37, and 38*, three sections perpendicular to the principal axis of such fruits, having the symmetry  $D_3$ ,  $D_5$  and  $D_6$  are drawn: here also the difference in the function of the binary axes for both cases, when  $n$  is *odd* or is *even*, is once more clearly demonstrated. As instances of objects having the symmetry  $D_n$ , attention may be drawn to the *propellers*, such as are used in aeroplanes, steamers, and in the laboratory as apparatus for the stirring of liquids. In *fig. 39* such a propeller, used as a stirrer in a thermostat, is shown in elevation; its symmetry is evidently  $D_4$ .

Fig. 39.  
Propeller.

In these cases too it is obvious that all objects and figures, having this particular kind of symmetry, may take a second form which is the mirror-image of the other. In the case of our stirrer, the one would correspond to a right-handed, the other to a left-handed screw.

§ 6. Up till now we have considered those figures which have one axis of the period  $\frac{2\pi}{n}$ , or such  $B'_c$

as possess two or more binary axes. The only case yet remaining is therefore that, where the figure has more than one axis with a period-number higher than 2. If this case too is treated in the most general way, we can really be sure that no other types of symmetry-groups only having rotations round axes of the first order, are omitted,

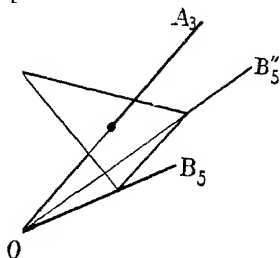


Fig. 40.

and that, therefore, the question of the possible groups of this kind has been finally and exhaustively settled.

Let us suppose that a figure possesses rotations round an axis  $A$  of the period  $\frac{2\pi}{n}$ , and also such round an axis  $B$  of the period  $\frac{2\pi}{p}$ . Remembering our previous conclusion that by the characteristic motions of the figure, it itself as well as its whole system of axes must be made to coincide with itself, it follows necessarily from this that round  $A$  there must be a number of  $n$  axes  $B$  equivalent to each other, and in the same way round  $B$  a number of  $p$  axes  $A$ , all of the same kind too. If a sphere with radius  $r$  be constructed round the fixed geometrical centre  $O$  of the figure, the points of intersection of all these axes  $B$  will be situated in the corners of a regular polygon with  $n$  sides, and those of the axes  $A$  in the corners of a regular polygon with  $p$  sides. As the whole system of axes must include a finite number of them, it is evident that all these points must be distributed over the whole surface of the sphere in such a way that all these polygons are arranged as the faces of a regular polyhedron, inscribed in the sphere, — the regular polyhedron formed by all the points  $A$  being the *polar figure* of the regular polyhedron formed by all points  $B$  as corners, and reversely. Now it is well-known, that there are only *five* possible regular, endospherical poly-



$ON$  coincides with  $ON'$ , and  $OP$  with  $OP'$ . Obviously this result could also be obtained if the figure were turned round an axis  $OS$  through  $180^\circ$ ;  $S$  is the point of intersection of two great circles joining  $N$  and  $N'$ , and  $P$  and  $P'$ , on a sphere whose centre is at  $O$ .

We can from this draw the general conclusion:

*If axes of period  $\frac{2\pi}{n}$  and  $\frac{2\pi}{p}$  be simultaneously present, there exist also binary axes, right in the middle of two axes of the same period.*

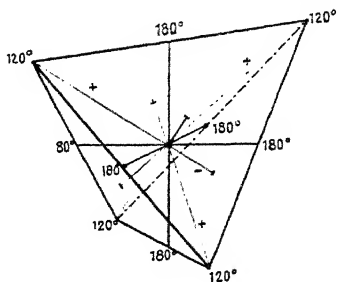


Fig. 42.

The theorem is quite general, and holds good also of the three regular polyhedra mentioned above.

§ 8. If the special symmetry of the three endospherical groups is reviewed, we can state the following:

a. There are figures which have the symmetry of the group  $T$ , including three homopolar binary axes perpendicular to each other and having the directions of the lines joining the middles of every two opposite edges of a regular tetrahedron; and four heteropolar ternary axes, having the direction of the four perpendiculars erected in the centres of each tetrahedron-face (fig. 42).

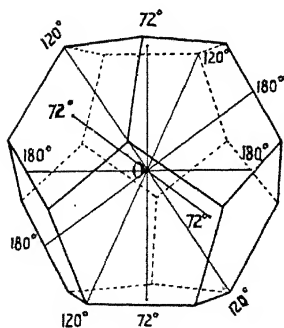


Fig. 43.

b. There are figures having the symmetry of the group  $K$ , including three perpendicular, homopolar, quaternary axes, having the direction of the perpendiculars in the centre of each cube-face; moreover, four homopolar ternary axes having the direction of the cube-diagonals; and six homopolar binary axes having the same direction as the lines joining the middles of every two opposite edges of the cube. (fig. 7).

c. There are figures possessing the symmetry of a group  $P$ , including six quinary axes having the directions of the perpendiculars in the centre of each face of a regular pentagonal dodecahedron; ten ternary axes having the directions of the lines joining every two most distant corners of

it; and fifteen binary axes having the directions of the lines joining the middles of every two opposite edges; all these axes are homopolar. (fig. 43).

§ 9. Finally it may be remarked that there exists an important theorem dealing with the number of non-equivalent, characteristic operations, making all symmetrical figures of these groups coincide with themselves. For the group  $T$  this number is evidently:  $1 + 3 + 4 \times 2 = 12$ ; for the group  $K$ :  $1 + 3 \times 3 + 4 \times 2 + 6 = 24$ ; for the group  $P$ :  $1 + 6 \times 4 + 10 \times 2 + 15 = 60$ ; the rotation through  $360^\circ$  is of course only counted *once* here.

Now the number of these non-equivalent operations is in every case  $= 2x$ , where  $x$  indicates the number of the edges of the tetrahedron, cube, or pentagonal dodecahedron respectively.

Indeed it appears to be a general property of each regular polyhedron with  $x$  edges, that it can be brought to self-coincidence in  $2x$  different ways.

This theorem is easily and quite generally demonstrable. It is connected with the simple fact that every edge  $AB$ , by interchange, can be placed so that its end  $A$  coincides with  $A$  or with  $B$  of any other edge present.

§ 10. Figures and objects of this kind are represented in fig. 44,

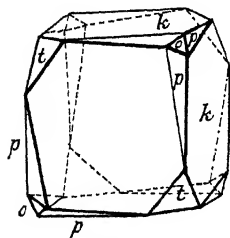


Fig 44.  
Barium-nitrate.

and 45. They give the crystal-forms of barium-nitrate:  $Ba(NO_3)_2$ , and of cuprite:  $Cu_2O$ , from Cornwall, —as illustrations of the symmetry of the groups

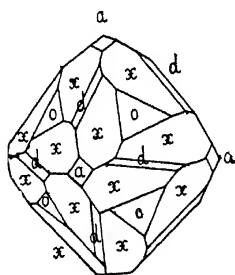


Fig. 45.  
Cuprite. (Cornwall).

$T$  and  $K$  respectively. The symmetry of the group  $P$  is not possible in the domain of crystalline matter, for a reason to be explained later on. Of course it needs no detailed discussion to see, that every figure of this kind may exist in a second form which is the mirror-image of the other one.

In the domain of living objects, a number of highly remarkable instances of all three groups  $T$ ,  $K$ , and  $P$ , are known. Indeed there is nothing to prevent the occurrence of the symmetry of group  $P$ , as there is with solid matter.

On the contrary, it seems that living objects show a certain preference for symmetry-axes of a period of  $\frac{2\pi}{5}$ .

As some interesting examples of this kind, we may mention the

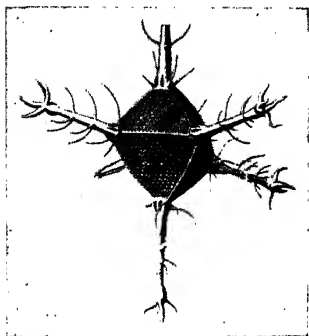


Fig. 46.

*Circoporus octahedrus*.

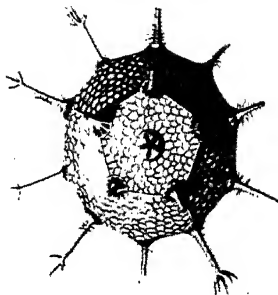


Fig. 47.

*Circorhegma dodecahedra*.

splendid forms of some *radiolaries* (*Phaeodaria*): of *Circoporus octahedrus* (fig. 46), of *Circorhegma dodecahedra* (fig. 47), and of *Circogonia icosahedra* (fig. 48), — all according to Haeckel's original descriptions; they are very striking instances of the symmetry of the groups *K* and *P* respectively, and these animals manifest in a most convincing way their morphological relations to the regular endospherical polyhedra, and more especially to the octahedron, the pentagonal dodecahedron, and the icosahedron.

As further instances of the group *K* we may mention from the same family of creatures: *Actinomma drymodes*, and *Asteracanthion*, after Haeckel's descriptions; of the group *P*: *Aulospaera icosahedra* in its youth-forms; etc.

In the vegetable world a certain number of pollen-cells seem to belong to these symme-

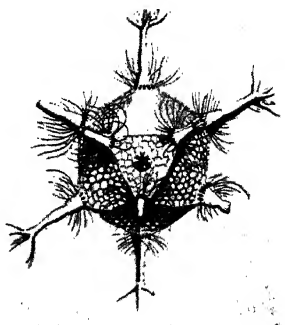


Fig. 48.

*Circogonia icosahedra*.

try-classes: to group *T* those of *Corydalis sempervirens*; and of group *P*, the pollen-cells of *Buchholzia maritima*, *Fumaria spicata*, *Polygonum amphibium*, *Rivina brasiliensis*, *Bannisteria versicolor*, etc. The number of these examples can certainly be augmented. Some of these pollen-cells are reproduced in fig. 49.

§ 11. As has been repeatedly stated, all forms and objects which show the symmetry of any of these groups possessing only

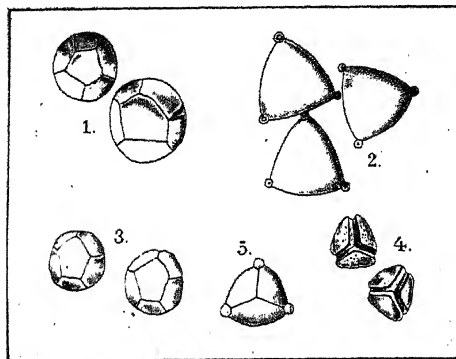


Fig. 49.  
Pollen-cells of

*Dianthus Cartusianorum* (1).

*Circaea alpina* (2).

*Rivina humilis* L. (3).

*Luzula campestris* (4).

*Mastixea arborea* (5).

axes of the first order, are different from their mirror-images. Of course all these

stereometrical figures and objects lack an inversion-centre, or, as is commonly said, they do not possess a symmetry-centre<sup>1)</sup>.

This is a fact which is of importance with respect to some physical properties, e. g., in the

case of crystals, as will be demonstrated more in detail later on

This fact of the occurrence of two different forms for every symmetrical object of this kind, which bear upon each other as mirror-images, is known as *enantiomorphism*; and both possible forms are called *enantiomorphous*.

The phenomenon of enan-

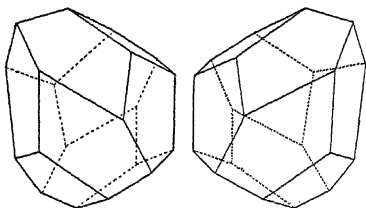


Fig. 50.

Right-, and left-handed  
deltoid-dodecahedron.

<sup>1)</sup> It may be remarked that the reverse of this conclusion is not generally true: from the absence of a symmetry-centre, enantiomorphism does not follow necessarily.

tiomorphism, and of enantiomorphous arrangements in space, is one of the most important facts in the whole domain of physical and chemical research, as we shall afterwards show in detail. In *fig. 50* the possible crystal-forms of some substances are reproduced as an illustration of two enantiomorphous polyhedra.

§ 12. With the aid of the devices employed in this chapter, we have succeeded in finding out all possible types of symmetrical groups of the first order; i. e. of all figures which can be made to coincide with themselves by *rotations alone*.

We can now use these groups, as we shall see, as a basis for the deduction of all those other groups which possess symmetry-properties of the second order too. This will be shown more exactly in the following chapter.



## CHAPTER IV.

*Some general Remarks on Axes of the Second Order. — Relations between Groups of the Second order and those treated in the previous Chapter. — General Theorems concerning Groups of the Second Order. Deduction of all possible Groups of this kind. — Summary.*

§ 1. We have now to consider such figures as have symmetry-properties of the second order as well as those that have of the first. For we have already seen that the existence of symmetry-properties of the second order necessitates the coexistence of those of the first too, unless the figure have a *single* axis of the second order only. This follows from the simple fact that every combination of two symmetrical operations of the second order is always equivalent to some rotation.

Besides this conclusion, we shall here-in after also make use of the fact already stated, that in many cases a mirror-axis may be replaced by a suitable combination of an axis of the first order with an inversion-centre or a plane of reflection.

Of course the most simple instances of groups of the second order will be those which are completely analogous to the cyclic groups in the previous chapter, but in this case having a single mirror-axis of the period  $\frac{2\pi}{n}$ . We shall call them *cyclic groups of the second order*, and give them the symbol  $\overline{C}_n$ , the horizontal line above the  $C$  indicating that the unique characteristic axis is now one of the *second* order. Before describing their general character, it will seem appropriate to extend our former considerations regarding the axes of the second order (see p. 23 to 25) to every arbitrary value of the period-number  $n$ .

§ 2. Let  $\overline{A}_n$  be an axis of the second order with a period  $\frac{2\pi}{n}$ .

If we remember its true characteristic operation, and the fact that *two* successive reflections in the same plane always neutralise each other, it must be immediately evident, that in the series of non-equivalent operations:  $\bar{A}(x)$ ,  $\bar{A}(2x)$ ,  $\bar{A}(3x)$ ... etc., only  $\bar{A}(x)$ ,  $\bar{A}(3x)$ ,  $\bar{A}(5x)$ ... etc., can be true operations of the second order, transforming the symmetrical figure  $F$  into its mirror-image  $F'$ . The others:  $\bar{A}(2x)$ ,  $\bar{A}(4x)$ ,  $\bar{A}(6x)$ ... etc., will be simple *rotations* round the axis  $\bar{A}_n$ , through angles  $2x$ ,  $4x$  etc.; that their number is evidently the same as that of the former ones, if  $n$  be an even number, needs no further comment.

From this consideration it is at once evident that there must be a difference between the cases when  $n$  is an *odd*, and when an *even* number. For if  $n$  is an odd number, the operation  $\bar{A}(nx)$  will be a mere reflection in a plane perpendicular to  $\bar{A}_n$ , because  $nx = 360^\circ$ , and the figure is transformed by this *odd* number of operations of the second order, into its mirror-image. The operation  $\bar{A}[(n+1)x]$  therefore will represent a pure *rotation*, equivalent to  $\bar{A}(x)$ , and thus will *not* be equivalent to any of the operations among the  $n$  first terms of the series. It follows from this that if  $n$  be an odd number, there are in the whole series  $2n$  non-equivalent operations present, of which  $n$  are mere rotations, and  $n$  true operations of the second order. Among these last ones there is present a *pure reflection* (namely  $\bar{A}(nx)$ ); and in consequence of a general theorem which will be discussed in § 3, the symmetry of the whole group may be defined also as the combination of certain rotations with reflections in a plane perpendicular to the axis  $\bar{A}_n$ .

If however  $n$  be an *even* number we may at once assume from the presence of the axis  $\bar{A}_n$ , that there are only  $n$  non-equivalent operations in the complete series. Half of them are rotations, and the other half are true, non-equivalent operations of the second order. It is also obvious that there is now *no* pure reflection present among the last ones; but *two* different cases must be distinguished here,  $\frac{n}{2}$  may be an *odd* or an *even* number.

If  $n$  be *even*, but  $\frac{n}{2}$  *odd*, evidently the term of the series  $\bar{A}\left(\frac{n}{2}x\right)$  will be a *pure inversion*, because it corresponds to the combination of the rotation through an angle  $\frac{n}{2}x = 180^\circ$ , with a reflection in a plane perpendicular to it; and as we have seen in the theorem on

page 15, this combination is always equivalent to an inversion. As a consequence of the same general theorem in § 3 mentioned above, we shall see that the symmetry of the whole group may therefore be also described as the combination of an axis of the first order  $A_{\frac{n}{2}}$ , with a period of  $\frac{4\pi}{n}$ , and a symmetry-centre.

The special example of  $n = 6$  in Chapter II was an illustration of this.

But if  $\frac{n}{2}$  be itself an *even* number, (i. e. if  $n$  itself be divisible by *four*), the term  $\overline{A}\left(\frac{n}{2}\alpha\right)$  is now equivalent to a simple *rotation* round the axis  $\overline{A}_n$  through an angle of  $180^\circ$ . Now as there is present among the operations of the group neither a pure reflection nor an inversion, the axis of the second order  $\overline{A}_n$  can in this case *not* be replaced by any combination of other symmetry-elements.

Some simple instances may make these facts more evident. If  $n = 4$ , we have the four non-equivalent operations:  $\overline{A}(90^\circ)$ ,  $\overline{A}(180^\circ)$ ,  $\overline{A}(270^\circ)$ , and  $\overline{A}(360^\circ)$ . From these the second and the fourth are equivalent to *pure rotations* through  $180^\circ$  and  $360^\circ$  respectively, because the figure is brought into positions in which it is congruent with itself. But  $\overline{A}(90^\circ)$  and  $\overline{A}(270^\circ)$  are true rotations round a *mirror*-axis. None of those four operations however is either a pure reflection or an inversion, and therefore the symmetry of the figure cannot be described in this case as any combination of an axis  $A_2$  or  $A_4$  with some symmetry-element of the second order. If  $n = 3$ , there are *six* non-equivalent operations:  $\overline{A}(120^\circ)$ ,  $\overline{A}(240^\circ)$ ,  $\overline{A}(360^\circ)$ ,  $\overline{A}(480^\circ)$ ,  $\overline{A}(600^\circ)$ , and  $\overline{A}(720^\circ)$ . From these the first, third, and fifth operations are true operations of the second order; but  $\overline{A}(240^\circ)$ ,  $\overline{A}(480^\circ)$ , and  $\overline{A}(720^\circ)$  are mere *rotations* round an axis  $A_3$ , through angles of  $240^\circ$ ,  $120^\circ$ , and  $360^\circ$  respectively. Among the three first mentioned operations,  $\overline{A}(360^\circ)$  is evidently equal to a *pure reflection* in a plane perpendicular to  $A_3$ . The whole symmetry of this group can therefore, according to the theorem dealt with in § 3 below, be described as the combination of a ternary axis  $A_3$  and a plane of symmetry perpendicular to it. The whole manner of argument is evidently always such, that not only the angle of rotation must be taken into account in the discussion, but also the special place which the operation considered occupies among the complete set of successive operations of the series: those with even number of succession are always pure rotations.

It may become clear from these instances also, that *the total number of non-equivalent operations of the second order which are present in such a group, is always the same as the number of rotations which it contains, the last ones always forming a closed group of rotations themselves*, in the sense in which the word "group" was defined in the previous chapter. The evidence of this will be seen from the simple observation that every two operations of the second order are together equivalent to some rotation which belongs to the characteristic ones of the group. The number of the operations of the second order which are non-equivalent, can therefore be neither greater nor smaller than the number of non-equivalent rotations, and thus must be equal to it. That these rotations themselves moreover form a closed group if the system be a *finite* one, is so obvious after all that has been said, that it needs no further comment.

*It will also be evident that the whole system of axes and symmetry-planes of the group will be brought to coincidence with itself by the action of every operation of the group, whether of the first or of the second order.*

§ 3. Now we can draw from all this a very important conclusion. Let  $Q$  be an arbitrary operation of the second order, characteristic for the group considered;  $\bar{A}(x), \dots \bar{A}(px)$ , etc., may be its non-equivalent rotations. If we combine all those rotations successively with  $Q$ , we shall obtain an equal number of non-equivalent operations of the second order, and as they will bring the whole system of symmetry-elements to self-coincidence, they will really, together with the equal number of rotations, constitute the *complete* group of the second order. If instead of  $Q$  we had chosen another operation of the second order characteristic of the group, the result would have been precisely the same; the only difference would appear in the succession of the non-equivalent operations of the second order, as it would result from the second mode of combination.

It follows from this: *that we can derive every group of the second order from one of the first order, by simply combining each of its typical non-equivalent rotations successively with one and the same operation of the second order  $Q$ .*

By this theorem the way is indicated by which we may come to the complete deduction of all possible symmetry-groups of the second order, starting from those which we met in the preceding chapter. It was this theorem we already mentioned in the beginning of this chapter, and which in future we shall also make frequent use of.

§ 4. The question may suggest itself: how can we be sure that the results will be *different* from each other if we combine a certain group of the first order  $G$  with an operation of the second order  $Q_1$ , and at another time with another operation of this kind  $Q_2$ ? Or in other words: when will the resulting groups of the second order  $\overline{G}_1$  and  $\overline{G}_2$  be different and when identical?

The answer is given by a general theorem which can without difficulty be proved to hold good in all cases: *In combining a group of the first order  $G$  with two different operations  $Q_1$ , and  $Q_2$  of the second order,  $\overline{G}_1$  and  $\overline{G}_2$  will be identical if the rotation which would be the result of combining  $Q_1$  and  $Q_2$  together, be already present among the characteristic non-equivalent rotations of the initial group  $G$ ; otherwise  $\overline{G}_1$  and  $\overline{G}_2$  will be really different from each other.*<sup>1)</sup>

The significance of this theorem will at once be apparent, because it gives a very simple criterion, whether, starting from a certain rotatory group  $G$  we must expect to find a *new* symmetry-group or a derived group identical with one already found on a former occasion.

§ 5. Now that these general theorems are known, we can resume our study of the groups  $\overline{C}_n$  again. From which precedes we may now readily conclude that:

a. If  $n$  be an odd number the symmetry of the group  $\overline{C}_n$  may be also described as resulting from the existence of an axis of the first order  $A_n$  with the same period as  $A_n$ , combined with a plane of symmetry perpendicular to  $A_n$ .

b. If  $n$  be an even number, but  $\frac{n}{2}$  odd, the symmetry of the group

1) The demonstration of this theorem can be given quite simply if we apply the method of Schoenflies here, who, following Jordan, Minnigerode and others, made use of the idea of the "multiplication of operations", after certain symbols for such operations are introduced, as they are used in the theory of groups.

Let  $Q_1$  and  $Q_2$  be the operations of the second order to be considered, e. g. inversions or reflections. The "product"  $Q_1 \cdot Q_2$  is now of course equivalent to a rotation  $A$ . Let us suppose it to be a rotation already present among those of group  $G$ . If we multiply the equation  $Q_1 \cdot Q_2 = A$  by  $Q_1$ , then, because  $Q_1^2$  is the identity, the result of this is:  $Q_2 = A Q_1$ . But  $A Q_1$  is an operation of the second order belonging to the new group  $\overline{G}_1$ , obtained from  $G$  by combination with  $Q_1$ ; thus the equation:  $Q_2 = A Q_1$  simply expresses that  $Q_2$  is also an operation of the second order characteristic of  $\overline{G}_1$ . But if so,  $\overline{G}_1$  would also have been obtained if  $G$  were combined immediately with  $Q_2$ ; instead of with  $Q_1$ ; i.e.,  $\overline{G}_1$  and  $\overline{G}_2$ , are identical.

may also be represented as resulting from the existence of an axis of the first order  $A_{\frac{n}{2}}$  with a period-number  $\frac{n}{2}$ , combined with a symmetry-centre.

c. If however  $n$  and  $\frac{n}{2}$  are both even numbers, the axis  $\bar{A}_n$  cannot be replaced by any other symmetry-element, or by any combination of them.

As some illustrations of figures and objects having the symmetry of the groups  $\bar{C}_6$ ,  $\bar{C}_3$ , and  $\bar{C}_4$  respectively, we give here in fig. 51, 52, and 53, the images of some polyhedra. The first represents the crystal-form of *diopase*:  $\text{CuH}_2\text{SiO}_4$ , and it is at once seen that the axis  $\bar{A}_6$  is, as an axis of the first order, only a ternary one, while

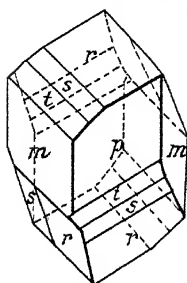


Fig. 51.  
*Diopase.*

an inversion-centre is combined with it.

Of the groups  $\bar{C}_3$  and  $\bar{C}_4$  we can only give some imaginary forms, because no real representatives of those groups have been found in the world of crystalline matter up to this date. But in any case it may be seen from these figures that

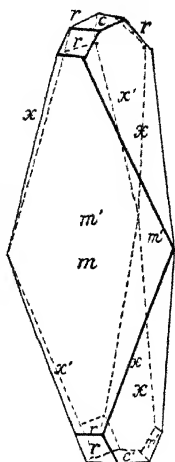


Fig. 52.

the symmetry of  $\bar{C}_3$  is the same, as if an axis of the first order  $A_3$  were present with a reflecting plane perpendicular to it. In the same way it will be obvious that in fig. 53 the special symmetry of the polyhedron cannot be described as any combination of axes and symmetry-properties of the second order, and can only be regarded as that of a true mirror-axis  $\bar{A}_4$  with a characteristic angle of  $90^\circ$ .

In the special case  $\bar{C}_n$ , where  $n$  has the value  $\infty$ , the symmetry of the figures is the same, as when a single plane of symmetry were present. Generally therefore the symbol  $S$  instead of  $\bar{C}_1$  is given to this group. This symmetry plays a predominant rôle in the description of a great number of living beings: many leaves, flowers, the bodies of innumeral animals of all kinds, etc., manifest this symmetry. In fig. 54 the crystal-form of *potassium-tetrathionate*:  $\text{K}_2\text{S}_4\text{O}_6$  has been reproduced; the plane of symmetry being placed here in a vertical position.

In morphology this important symmetry is commonly regarded as that of *bilateral-symmetrical* forms. As such, innumerable leaves

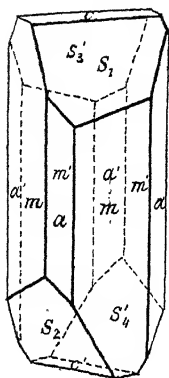


Fig. 53.

(vine, oak, etc.), and flowers (*Papilionaceae*, *Orchidaceae*, *Labiates*, of *Fumaria*, etc.) are representatives of this class. In fig. 55 some flowers of this kind: *Paphiopedilum Hookerianum* (d); *Galeopsis dubia* (a); *Lamium purpureum* (b); *Brunella grandiflora* (c); *Dalhousiea bracteata* (e); *Cyclopia genistoides* (f); *Podalyria cordata* (g), have been reproduced

as typical examples of the said symmetry, to bring back this well-known fact to memory.

It may be remarked here as a very important fact that almost all the higher living beings (man, quadrupeds, birds, insects, etc.) have the symmetry of the group *S*, being a single plane of reflection their only symmetry-element. The lower animals on the contrary (*Blastoidea*, *Coralla*, *Radiolariae*, *Discomedusea*, *Ascidiae*, etc.) often show a much higher symmetry characterised by axes of high period-numbers ( $n = 4, 5, 6$ , etc.), and by the presence of several planes of symmetry. In this respect it would appear as if a striking contrast were present in the evolutionary development of living and of so-called inanimate matter. For in the domain of crystallography generally the holohedral classes of each system show an incomparably

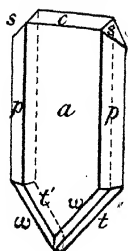
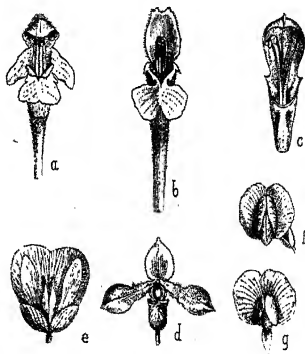
Fig. 54.  
*Potassium-tetrathionate.*

Fig. 55.

a. *Galeopsis dubia*. b. *Lamium purpureum*. c. *Brunella grandiflora*. d. *Paphiopedilum Hookerianum*. e. *Dalhousiea bracteata*. f. *Cyclopia genistoides*. g. *Podalyria cordata*.

greater number of representatives than the hemihedral and tetartohedral classes, and it was therefore suggested by some crystallogra-

phers that hemihedral development might only be a result of particular circumstances during the growth of the crystal, — a view which can, however, hardly be thought justified. As we shall see later, crystals have in many cases also a tendency to syncrystallise in apparently higher symmetrical aggregations than they are themselves, and thus often to imitate a symmetry of the composed individual obtained by polysynthetic twinning, much higher than its own.

In living nature on the other hand, it seems that the morphological evolution goes in the direction from higher to lower symmetry.

Whether it be so or otherwise: in any case the fact of the numeral occurrence of the bilateral symmetry among higher animals has not yet been explained in a rational way. Although therefore the deeper causes of this phenomenon are not yet known, suspicion arises that they are in some way connected with the particular circumstance of *animal motion*. Among the lower beings there are many, of which a *sedentary* life is characteristic; and it may be of advantage for the purpose of nutrition, etc., for the living being, to be in contact with its environment in as many directions as is possible. Evidently the symmetrical repetition of parts or organs of its body, is a way of accomplishing this. In general the immobility of the living organism is a factor much more compatible with the real character of symmetry than motion is. For that reason the organs of plants are arranged as a whole with higher symmetry, and are also more symmetrical in themselves than those of the animals, while the most perfect symmetry finally is manifested in the forms of immobile, *crystallised* matter. On the other hand, for the animals which can move freely, the best mechanical stability may have been a reason of importance in the development of their somatic forms.<sup>1)</sup>

Finally, if  $n = 2$ , the symmetry of the group  $\overline{C}_n$  consists in the presence of the *inversion* as the only symmetry-property.

Such figures have thus only a centre of symmetry. As an instance of this kind every crystal-form of a holohedral triclinic crystal, e.g. of *copper-sulphate* ( $+ 5H_2O$ ) in *fig. 56*, can be mentioned. It is more difficult to find examples of living beings showing the symmetry of this group  $\overline{C}_2$ , which is commonly indicated by the symbol *I*.

<sup>1)</sup> Cf. F. M. Jaeger, Over Kristallografische en Moleculaire Symmetrie van plaatsings-isomere Benzol-derivaten, Dissertatie *Leiden*, (1903), p. 202—208; Zeits. f. Kryst. **38**. 592. (1904).



Perhaps some representatives of the family of the *radiolaries*, as e. g., *Aulosphaera elegantissima*, may be conjectured to possess this symmetry.

§ 6. Proceeding with the deduction of the possible groups of the second order, we can now start with those groups  $C_n$  of the first order dealt with in the previous chapter, which only possess a single heteropolar axis of the first order, and combine these groups  $C_n$  with a typical symmetry-element of the second order in the way formerly discussed.

As we have seen, we can use for that purpose either the reflection

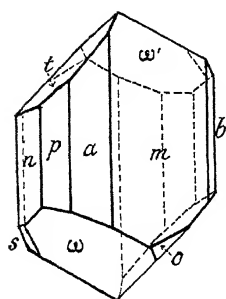


Fig 56.

Copper-sulphate ( $5H_2O$ ).

in a plane, or the inversion, because the simultaneous presence of *several* axes of the second order always involves the coexistence of rotations, and thus can be reduced to the cases in which these rotations are combined with reflections or with the inversion. For if not so, the simultaneous addition of several axes of the second order to a rotation-group, would in general imply the formation of other axial combinations than those already deduced in the preceding chapter, and this is impossible. The axes of the

second order in groups of the second order, if present therein at all, can therefore only coincide with the axes of the first order, because each axis of the second order is at the same time always also one of the first order. The only question is therefore: in what way must these planes of reflection or this symmetry-centre be combined with  $C_n$ ?

Of course this must happen in such a way that the whole axial system of the group will coincide with itself by the operation which results from the addition of the new symmetry-element. In the case where only a single axis  $A_n$  is present, as in our groups  $C_n$ , this can evidently be the case only if the added plane of symmetry  $S$  be either perpendicular to the axis  $A_n$ , or passes through that axis.

If we suppose  $A_n$  to be in a vertical position, we can indicate both kinds of reflections by  $S^H$  (horizontal reflecting plane) and by  $S^V$  (vertical reflecting plane), and we have now only to investigate if the groups of the second order thus obtained:  $C_n^H$ ,  $C_n^V$ , and in the case of the addition of the symmetry-centre:  $C_n^I$ , are identical or different groups.

To answer the last question we have simply to investigate what will be the result of the combination of the operations  $S^H$ ,  $S^V$ , and  $I$ , taken two at a time. Now  $S^H$  and  $S^V$  together will be equivalent to a rotation through  $180^\circ$  round a *horizontal* axis;  $S^V$  and  $I$  combined, too. But the combination of  $S^V$  and  $I$  will be equivalent to a rotation through  $180^\circ$  round a *vertical* axis, and this operation will be present or not present among the rotations of  $C_n$ , according as  $n$  is either an *even*, or an *odd* number itself. If therefore  $n$  be an *even* number, the combination of  $C_n$  with  $S^H$  or with  $I$  will give *identical* results: in this special case the groups  $C_n^H$  are identical with  $C_n^I$ , according to the theorem mentioned above. If however  $n$  be *odd*, we shall have three kinds of new groups of the second order.

But it will be obvious, in connection with what was said in the discussion of the groups  $\overline{C}_n$ , that some of the groups here considered are the same as several of the type  $\overline{C}_n$ . For if  $n$  be *odd*,  $C_n^H$  is evidently the same as  $\overline{C}_n$ ; and therefore in this case the symmetry of the figure can be expressed as well by the symbol  $\overline{C}_n$ , as by  $C_n^H$ .

To sum up the above results, we can say:

*a. There are figures possible whose symmetry is characterised by the presence of a single axis  $A_n$  of the first order, and by  $n$  planes of symmetry passing through it.<sup>1)</sup> The symbol of these groups is  $C_n^V$ ; their principal axis is a heteropolar one, as well as in the case of the cyclic groups  $C_n$  themselves.*

*b. There are a number of figures, the symmetry of which consists in the existence of a single homopolar axis  $A_n$  of the first order, and a plane of symmetry perpendicular to it. Their general symbol is  $C_n^H$ . If  $n$  be *odd*, these groups are identical with  $\overline{C}_n$  for the same value of  $n$ ; if  $n$  be *even* however, they also possess a symmetry-centre, because they are identical with the groups  $C_n^I$  for the same values of  $n$ .*

*c. Other groups with one single axis  $A_n$  of the first order are impossible; for  $C_n^I$  is for odd  $n$  identical with  $\overline{C}_{2n}$ , and for even  $n$  with the groups  $C_n^H$ . If more axes of the second order were however present, the groups would possess more than a single axis, and such groups of course do not belong to the kind here considered.*

**§ 7.** It is of interest to look here for some representatives of the discussed types of symmetrical objects, before we continue

<sup>1)</sup> If one plane passes through an axis  $A_n$ , there are  $n$  such planes passing through it. This needs no further comment after what precedes.

our systematical deduction of the other groups of the second order.

The symmetry of the type  $C_n^V$  plays a very important rôle in nature,

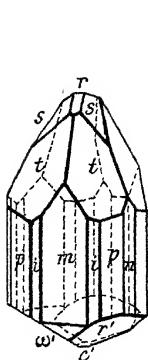


Fig. 57.  
*Turmaline.*

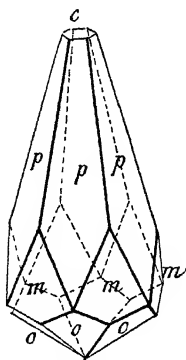


Fig. 58.  
*Silver-iodide.*

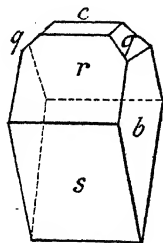


Fig. 59.  
*Struvite.*

and more particularly among living beings; but there are also many representatives of it known among the forms of crystalline matter.

As instances of this kind, in *fig. 57, 58, and 59*, the crystal-forms of *turmaline* ( $C_3^V$ ), of *silver-iodide*:  $AgI$  ( $C_6^V$ ), and of *struvite*:  $Mg(NH_4)PO_4 + 6H_2O$  ( $C_2^V$ ), are reproduced here.

In all these figures the prominent feature of the *hemimorphic* development is immediately seen; indeed, this peculiarity of their external shape is one of the most characteristic things about crystals of this kind, just as in the cases of  $C_n$ .

In living nature, the type of symmetry mentioned is one of those most frequently occurring. As instances in botany, we have reproduced here in *fig. 60* some fruits and flower-diagrams which manifest this symmetry very strikingly indeed. So in *fig. 60* there is reproduced a fruit of *Bignonia echinata*.

(Gaertner), which shows the symmetry of group  $C_2^V$ .



Fig. 60.  
Fruit of  
*Bignonia echinata.*

The blossoms of many *Cruciferae*, of *Circaea lutetiana*, of *Fraxinus*, etc., evidently belong to the same class also.

In the domain of animal life we can mention as representatives of this symmetry, a number of *Ascidiae*: *Polyclinum constellatum*; of *radiolaries*; *Spyridibotrys trinacria*. The polar nature of the principal axis of all these objects is clearly noticed in the examples chosen.

Of the group  $C_2^F$  we have in fig. 61 reproduced the fruit of *Gloriosa superba*, in fig. 62 that

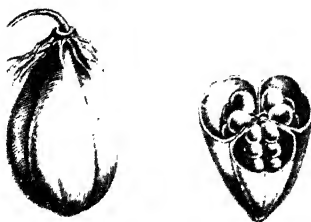


Fig. 61.

Fruit of *Gloriosa superba*.

of *Canarium decumanum*, after Gaertner. Also the blossoms of *Camphora officinarum*, of *Hydrocharis*, and of *Triglochin maritimum*, are instances of this kind.



Fig. 62.

Fruit of  
*Canarium decumanum*.

In fig. 1 on Table I (p. 64) we have reproduced the beautiful forms of *Porites furcata* (Haeckel), one of the class of *Hexacoralla*, which are celebrated for their graceful forms; and also of the *Ascidiae*: *Botryllus polycyclus* (fig. 2). The symmetry of the group  $C_4^V$  is met with in many *Discomedusae*: also we can find it in the mantles of *Pelagia perla*, of *Drymonema victoria* (fig. 3), and in the stomach-section of *Undosa undulata* (fig. 5), according to Haeckel's drawings, (Table I). *Cyanea aurelia* too, and many other jellyfishes, show this symmetry in a very striking way. Among the *Ascidiae*, the mantle of *Botryllus Marionis* (fig. 4, Table I) may

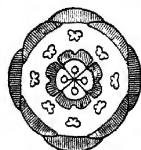


Fig. 63.

Blossom-diagram of  
*Aspidistra elatior*.

be considered as an example of this kind.

Further, in fig. 63 the blossom-diagram of *Aspidistra elatior* is

reproduced, which too manifests this particular symmetry very beautifully. Another instance is the diagram of *Daphne Mezereum*.

Of group  $C_2^V$  innumerable representatives are found in living nature, as well among plants as animals. It even seems that a certain preference for this special symmetry may be supposed to exist, which is the more remarkable, because exactly this symmetry is quite impossible for crystalline matter. In fig. 64 the fruits of *Swietenia mahagoni*, in fig. 65 that of *Ceiba pentandra*, and in fig. 66 that of *Adansonia Baobab*, all after Gaertner, are reproduced here as good examples of this class. Of blossom-diagrams we draw attention to the corolla of *Campanula medium*, and of *Platycodon grandiflorus*, both in fig. 67.

Other instances are the diagrams of *Carduus crispus*, of *Cucurbita pepo*, of *Hedera helix*, etc.

Among the lower animals the most beautiful instances of this symmetry-class are found in



Fig. 65.  
Fruit of  
*Ceiba pentandra*.

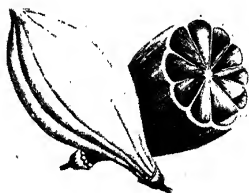


Fig. 66.  
Fruit of *Adansonia Baobab*.

the *Blastoidea*, some of which are reproduced in fig. 6—9 on Table I (p. 64). The lime-armour of *Orophocrinus stelliformis* (fig. 9), of *Pentremites orbignyannus*, (fig. 8) of *Phaenoscisma acutum* (fig. 7), and that of *Asteroblastus stellatus* (fig. 6) are, according to Haeckel's drawings, splendid illustrations of this kind. Finally we must not forget the well-known forms of the star-fishes, e. g.,

*Asteria ruber* (fig. 68), as they are found all along our sea-shores.

The symmetry of the group  $C_6^F$  is also met with very often in nature.

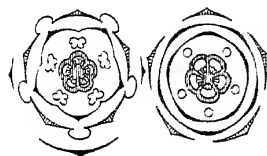


Fig. 67. Blossom-diagrams of *Campanula medium* and *Platycodon grandiflorus*.

Among the lower animals the most beautiful examples are found in the *Hexa-*

*coralla*; especially the lime-formations of *Cyathina cylindrica*, *Stephanophyllia complicata* and *elegans* (fig. 12 on Table I), of *Astrocyathus paradoxus* (fig. 10, Table I) etc., are according to Haeckel's drawings, good illustrations of this symmetry and excellent instances of these



Fig. 69. Blossom-diagram of *Cephalotus follicularis*.

pretty forms. In fig. 69 moreover the blossom-diagram of *Cephalotus follicularis* has been reproduced, while in fig. 70 a drawing of the fruit of *Aubletia caseolaris* is given (after Gaertner), and in fig. 71 a fruit of *Badamia Commersoni*, both as good botanical examples of this same symmetry.

It seems that also among the *Ascidiae* some representatives of this class are found: evidently *Molgula tubulosa*, and *Synoecum turgens* may be reckoned among this kind of symmetrical objects.

Of the groups with an axis  $A_n$  of higher value for  $n$  than 6, it is not easy to find good

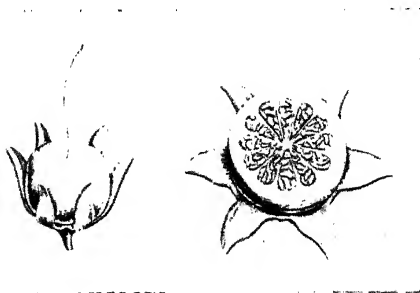


Fig. 70. Fruit of *Aubletia caseolaris*.

examples in nature. Perhaps among the *Hexacoralla* the form of

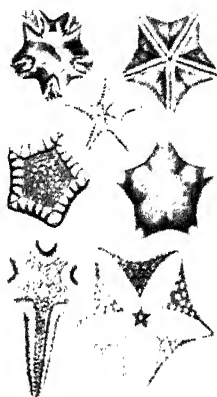


Fig. 68. *Asterias ruber*.

*Leptocyathus elegans* (Haeckel) may be mentioned as a representative of the group  $C_2^V$ .

Of the groups  $C_n^H$ , which of course give only a series of new forms for even values of  $n$ , no instances among plants and animals have been found up till now.



Fig. 71.  
Fruit of *Badamia Commersoni*.

As an illustration of some

kind, in fig. 72 and 73 the crystal-forms are reproduced of *scheelite*: ( $C_4^H$ ), and of

( $C_6^H$ ); these figures show the respective symmetries rather clearly. Of course the heteropolar character of the principal axis has here disappeared; and from the figures reproduced it may be obvious that the polyhedra under consideration possess really a symmetry-centre.

The symmetry of the group  $C_2^H$  is very often met with in the case of crystalline substances: all so-called *monoclinic* substances, the number of which is extremely great, belong to this group, as far as they are holohedral.

Commonly the horizontal plane of symmetry is placed vertically in figures of this kind, so that the binary axis now will have a horizontal

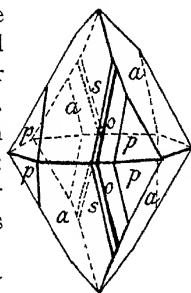


Fig. 72.  
*Scheelite*.

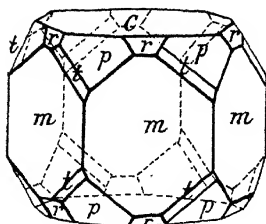


Fig. 73.

direction. This custom is followed also in the accompanying drawing (fig. 74) which represents a crystal of the mineral *amphibole*:

$p \text{ Ca(Mg,Fe)(SiO}_3)_2 + q \text{ MgAl}_2\text{SiO}_6$   
in various proportions  $p$  and  $q$ .

§ 8. The remaining groups of the second order yet to be dealt with, are related to the *dihedron*-groups  $D_n$ , or to the *endospherical* groups  $T$ ,  $K$ , and  $P$  respectively.

Let us start with those which are related to  $D_n$ , and which

therefore have a homopolar principal axis  $A_n$  and  $n$  binary axes situated in a plane perpendicular to  $A_n$ , and are either homopolar, but of two different sets, or heteropolar and of the same set (p. 38).

We must now add reflections  $S$  or an inversion  $I$  to the groups  $D_n$ ; in every case the whole system of axes of  $D_n$  must coincide with itself by the operations corresponding to the symmetry-elements added. Therefore the following cases must be taken into account: the added plane of reflection may be either *horizontal*:  $S^H$  or *vertical*  $S^V$ , and this last may pass *through* the binary axes themselves, or may *bisect* the angle  $\frac{n}{n}$

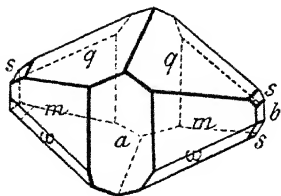


Fig. 74.

*Amphibole.*

between two successive binary axes.

In the first case we shall call it  $S^V$ , in the other case  $S^D$ , to symbolise the "diagonal" situation of it. Altogether we have now to discuss the addition to  $D_n$  of the operations:  $S^H$ ,  $S^V$ ,  $S^D$ , and  $I$ .

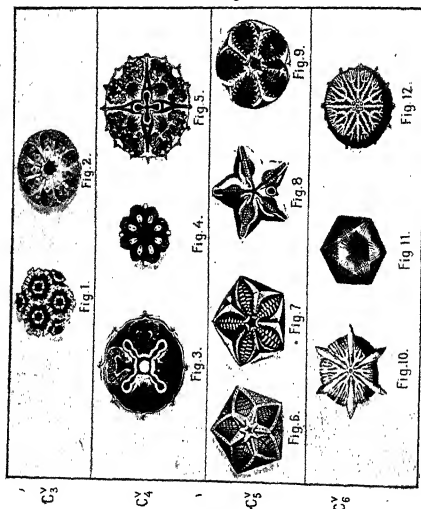
The operations  $S^H$  and  $S^V$  are *together* equivalent to a rotation through  $180^\circ$  round a binary axis, already found among the axes of the group  $D_n$ . Therefore in every case the result of combining  $D_n$  either with a horizontal plane of reflection, or with a vertical one passing through a binary axis, will always be *the same*.

However, if we combine  $S^H$  and  $S^D$ , the result will be equivalent to a rotation round a binary axis, bisecting the angle between two successive binary axes of the group  $D_n$  already present. And as such rotations are not yet included among those of the group  $D_n$ , the groups  $D_n^H$  and  $D_n^D$  will be always *different* from each other.

The combination of  $S^H$  and  $I$  is equivalent to a rotation through  $180^\circ$  round an axis coinciding with the principal axis  $A_n$ . This rotation is present or absent among those of  $D_n$ , according as  $n$  is an *even* or an *odd* number. Therefore, if  $n$  is *even*,  $D_n^H$  and  $D_n^I$  will be *identical* groups; only for  $n = \text{odd}$  number, the combination with a symmetry-centre would produce a new group  $D_n^I$ , which might appear different from any till now deduced. However on closer examination it becomes obvious that it is identical with the groups  $D_n^D$  already mentioned for *odd* values of  $n$ , because the inversion and every binary axis together will produce a plane of symmetry perpendicular to the last one. We can thus include all cases in the combinations of  $D_n$  with  $S^H$  and  $S^D$ , and it is no longer necessary

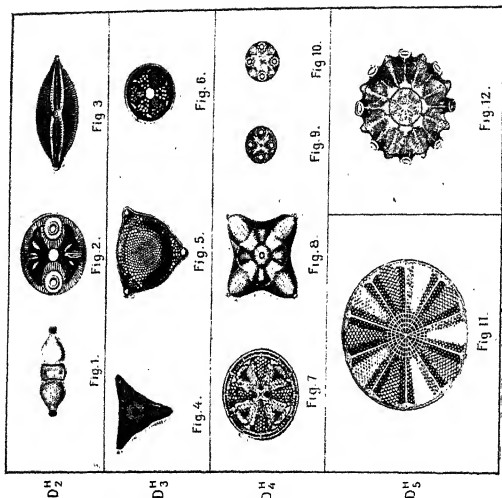


TABLE I.



1. *Porites furcata*. 2. *Botryllus polycyclus*. 3. Mantle of *Drymonema victoria*. 4. Mantle of *Botryllus Marionis*. 5. Stomach of *Undosa undulata*. 6. *Asteroblastus stellatus*. 7. *Phaenoscisma acutum*. 8. *Pentremites orbigenyanus*. 9. *Orophocrinus stelfiformis*. 10. *Astrocyathus paradoxus*. 11. *Thamnastraea arachnoides*. 12. *Stephanophyllia elegans*.

TABLE II.



1. *Biddulphia pulchella*. 2. *Auliscus elegans*. 3. *Navicula dichyma*. 4. *Triceratium digitale*. 5. *Triceratium Robertsonianum*. 6. *Actinophycheus constellatus*. 7. *Actinophycheus heliopolita*. 8. *Amphithelaeus elegans*. 9. *Auliscus crucifer*. 10. *Auliscus cratijer*. 11. *Aulacodiscus Grenitcanus*. 12. *Groeva pedalis*.

to consider the combination with  $I$ . Although we might stop here, as the combinations with  $S^H$ ,  $S^D$ ,  $S^F$ , and  $I$  have now been sufficiently discussed, it may yet be of interest to extend these discussions. Of course it will then appear, that really *no* new groups can be produced beyond those already mentioned.

For this purpose let us first investigate the combination of  $S^F$  and  $S^D$ . This combination will be equivalent to a rotation round an axis  $A_n$  through an angle which is *double* that between  $S^F$  and  $S^D$ , i. e. through an angle  $\frac{2\pi}{n}$ . As this rotation is not yet included among those characteristic of  $D_n$ , — because the angle of rotation corresponding to  $A_n$  is  $\frac{2\pi}{n}$ , — the groups  $D_n^D$  and  $D_n^F$  will really be different. But  $D_n^F$  need not be considered because we found it identical with  $D_n^H$ ; so it is once more confirmed, that  $D_n^H$  and  $D_n^D$  are really *different* from each other.

Similarly  $S^F$  and  $I$  are together equivalent to a rotation through  $180^\circ$  round a binary axis perpendicular to  $S^F$ . As  $S^F$  passes through a binary axis of  $D_n$ , the resulting binary axis will be perpendicular to one of the binary axes characteristic for  $D_n$ . If  $n$  be *even*, such an axis perpendicular to one of the other binary axes will be found already among those of  $D_n$ . If  $n$  be *odd*, this would *not* be the case. Therefore only if  $n$  is an *odd* number, will the groups  $D_n^F$  and  $D_n^I$  be different; but  $D_n^F$  being for *all* values of  $n$  the same as  $D_n^H$ , it is only demonstrated here once more that  $D_n^H$  and  $D_n^I$  are wholly *identical* for *even* numbers  $n$ , and *only different* if  $n$  is an *odd* number. But, as we have seen, for  $n = \text{odd}$ ,  $D_n^I$  is identical with  $D_n^D$  already deduced.

Finally we have to consider the last possible combination: that of  $S^D$  and  $I$ . The result of both is a rotation through  $180^\circ$  round a binary axis perpendicular to  $S^D$ . Now, if  $n$  is *odd*, such binary axes will already have been found among those of  $D_n$ ; if however  $n$  be *even*, it will be a new one with respect to the binary axes of  $D_n$ . From this it follows that only for  $n = \text{even}$ , can the deduced groups  $D_n^D$  and  $D_n^I$  be *different* from each other. But if  $n$  is an *even* number,  $D_n^I$  will be always the same as  $D_n^H$ ; so that our result amounts to saying that for *even*  $n$  the groups  $D_n^D$  and  $D_n^H$  will yet differ, — just as we have already stated. Since, because for *odd*  $n$ ,  $D_n^I$  is certainly different from  $D_n^H$ , it is here once more demonstrated that in *all* cases  $D_n^H$  and  $D_n^D$  must be different from each other.

In this connection it is of importance to draw attention to a special property of the axis  $A_n$  if such a dihedron-group  $D_n$  is made into one of the second order by adding a diagonal mirror-plane  $S^D$  to it. It can easily be proved by means of group-theoretical argumentations that *in this case* the axis  $A_n$  is transformed at the same time into an axis  $\bar{A}_{2n}$  of the second order <sup>1)</sup> with a period of  $\frac{\pi}{n}$ .

In this way we see the combination of an axis of the second order appear, besides the planes of symmetry, within the scope of our deductions; the combination mentioned evidently proves to have significance only for an *even* period of the axis of the second order.

§ 9. If therefore we review the results obtained by these considerations, we can maintain generally that all possible groups of the second order which are directly related to the dihedron-groups of the previous chapter, can be deduced from them by combination with  $S^H$  or  $S^D$ , — the last mentioned combination making the principal axis  $A_n$  simultaneously into an axis  $\bar{A}_{2n}$  of the second order, with a period-number  $2n$ .

Therefore:

*There are symmetrical figures which possess the axial system of the groups  $D_n$ , with a horizontal plane of symmetry perpendicular to the principal axis  $A_n$ , and thus containing all binary axes; moreover they possess  $n$  vertical planes of symmetry passing through  $A_n$  and every binary axis. If  $n$  is an even number, there will be also a symmetry-centre present; if  $n$  be odd, however, the figure will have no centre of symmetry. The symbol of these groups shall be  $D_n^H$ .*

*b. There are symmetrical figures which possess the axial system of the groups  $D_n$ , with a system of  $n$  vertical planes of symmetry passing through the principal axis  $A_n$ , and bisecting the angles between every*

<sup>1)</sup> For the general and simple demonstration of this theorem, the same symbols for the "multiplication" of operations of the first and second order can be used as we drew attention to previously. Let  $SD$  be the diagonal plane bisecting the angle  $\frac{\pi}{n}$  between two successive binary axes of  $D_n$ , and let  $A_2$  be a rotation through  $180^\circ$  round such an axis;  $SH$  and  $SV$  may be positions of planes of reflection, as we have defined them in § 8 of this chapter. Then we have:  $A_2 = SH.SV$ , and therefore  $A_2.SD = SH.SV.SD$ . Now  $SV.SD$ , including an angle  $\frac{\pi}{2n}$  of course, will be equivalent to a rotation round an axis of the same direction as the principal axis  $A_n$  of the group  $D_n$ , but through the *double* angle  $\frac{\pi}{n}$ . The operation  $A_2.SD$  of the new group is thus evidently equivalent to  $SH.A(\frac{\pi}{n})$ , i. e. to the rotation round a *mirror-axis* with a period-number  $2n$ . Thus the above-mentioned theorem is generally proved.

two successive binary axes. If  $n$  be an even number, the figure will have no symmetry-centre; if however  $n$  be odd, the group will certainly possess such a centre too. In every case the principal axis  $A_n$  will be simultaneously an axis  $\bar{A}_{2n}$  of the second order with a period-number  $2n$ . The symbol of these groups shall be  $D_n^D$ .

§ 10. The symmetry of the groups  $D_n^H$ , both for even and for odd values of  $n$ , is often met with in nature.

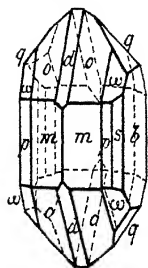


Fig. 75.  
Olivine.

As instances of this kind in polyhedral forms, in fig. 75 the crystal-form of the orthosilicate *olivine*:

$(Mg, Fe)_2SiO_4$  is reproduced as a representative of the group  $D_2^H$ , while, as up till now no natural representative of the class  $D_2^H$  among crystals is known, an imaginary polyhedron, having this symmetry, is

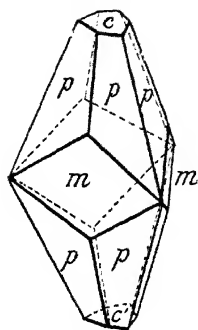


Fig. 76.

drawn in fig. 76. The figures which possess a symmetry  $D_2^H$ , have three binary axes perpendicular to each other, and three planes of symmetry, each containing two of these binary axes. All so-called orthorhombic (holohedral) crystal-forms, which are extremely numerous, belong to this class.

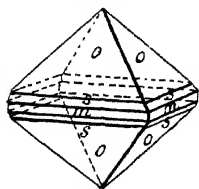
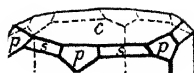


Fig. 77.  
Zircon.

In fig. 1—12 of Table II a number of instances of these groups among plants and animals are reproduced: so we find here the beautiful silica-structures of



$m$   $|m|$



Fig. 78.  
Beryll.

*Diatomeae*: if they be considered similarly developed at their tops and bases <sup>1)</sup>, they may be mentioned indeed as very striking examples of the symmetries:  $D_2^H$ ,  $D_3^H$ ,  $D_4^H$  and  $D_5^H$ , and perhaps also of  $D_8^H$ , in their most elegant shapes.

<sup>1)</sup> If the upper and basal parts of the silica-boxes are thought to be different, the axis  $A_n$  will then be heteropolar, and the symmetry will be simply that of the groups:  $C_n^V$ .

As illustrations we have chosen here the following representatives of these two classes: Of the group  $D_2^H$ : *Biddulphia pulchella* (fig. 1); *Auliscus elegans* (fig. 2); *Navicula dichyma* (fig. 3); of the group  $D_3^H$ : *Triceratium digitale* (fig. 4), and *Robertsianum* (fig. 5); *Actinoptychus constellatus* (fig. 6).

Of the groups  $D_4^H$  and  $D_6^H$  we have chosen as examples the crystal-forms of *zircon*:  $ZrSiO_4$  (fig. 77;  $D_4^H$ ), and of *beryll*:

$Be_3Al_2(SiO_3)_6$ , (fig. 78;  $D_6^H$ .)

On Table II moreover the following objects have been reproduced of  $D_4^H$ : *Actinoptychus heliopelta* (fig. 7); *Amphiheltras elegans* (fig. 8); *Auliscus crucifer* (fig. 9) and *eratif* (fig. 10). Of the group  $C_3^H$  only *Aulacodiscus Grevilleanus* (fig. 11); a very fine specimen of this symmetry being also *Triceratium pentacrinus*, which is however not reproduced here. The form of *Groeca pedalis* (fig. 12) on the contrary may be looked upon as an illustration of the group  $D_8^H$ , whose representatives are very rare. Most of these figures were reproduced after Haeckel's original drawings.

Of the group  $D_6^H$  no instances have been found among the *Diatomeae*; but perhaps some *radiolaries* may belong to this class: so *Ethmosphaera siphonophora* (Haeckel). If the top and the basal parts of the fruit of *Badamia Commersoni* (fig. 71) were equally developed, — which is certainly not the case however, — this form would give an idea of a vegetable object possessing this symmetry.

Some pollen-cells, e.g. those of *Passiflora angustifolia*, *Heliotropium grandiflorum*, etc., may be reckoned, according to some authors, to have this symmetry too.

The *spicula* of a number of *radiolaries* are arranged in a regular and most remarkable way. This special regularity was already described by Joh. Müller, and defined by him in a "rule" which bears his name. The particular symmetry of this arrangement appears to be that of the group  $D_4^H$ ; as in the case of *Acanthostaurus*, *Acanthometra*, etc. The pollen-cells of *Annona tripetala* seem to belong here too.

A striking example of the symmetry  $D_3^H$  in the case of *radiolaries*, is that of *Acanthodesmia prismatium* (fig. 79), after Haeckel's drawing.

Haeckel was one of the first to understand the eminent value of the principle of symmetry for the description of plants and animals, and to draw special attention to the symmetrical and highly aesthetic forms of the lower beings in his great work on the *Radiolaries*, and in his book: "*Kunstformen der Natur*".

This author<sup>1)</sup> also made the first valuable attempts to found a system of morphological description on the base of the symmetry-principle. However he could *not* succeed in this, because an exact treatment of the symmetry-problem had not yet been made, or at least was not known to him. Without wishing to belittle his work, we feel compelled in the light of our more modern conceptions, to reject his system, and replace it by the one developed here in detail.

It should be remarked *that of course not only an organism as a whole, but also every part of it may be morphologically described by means of the principles here developed.*

Thus the corolla of a flower can have a symmetry  $C_6$ , its calyx that of group  $S$ , its pistil of  $C_3$ , its ovary of  $C_5$ ; etc.

By simply writing down the symbol of its symmetry-group, as adopted here, it is possible to characterise every form in the most concise manner.<sup>2)</sup>

As instances of the symmetry  $D_2^D$  and  $D_3^D$ ,

in fig. 80 and 81 the crystal-forms are reproduced of *chalcopyrite*:



Fig. 79.

*Acanthodesmia prismatium.*

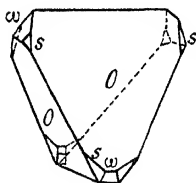


Fig. 80.

*Chalcopyrite.*

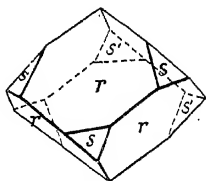


Fig. 81.

*Calcite.*

<sup>1)</sup> E. Haeckel, *Systematische Phylogenie*; Entwurf eines natürlichen Systems der Organismen auf Grund ihrer Stammesgeschichte, Bnd. I—III Jena, (1894). He speaks of four principal classes of forms: *Centrostigma*, *Centroaxonia*, *Centroplana*, and *Anaxonia*. A comparison with our results must readily convince everybody that in his system a confusion of all classes is present.

<sup>2)</sup> It must be remembered here that, from a historical viewpoint, the zoologist Gust. Jäger had before Haeckel already made such attempts in this direction, without however publishing a complete system of classification based upon the symmetry-principle.

$\text{CuFeS}_2$ , and one of the numerous forms of *calcite*:  $\text{CaCO}_3$ . In both cases it may be seen that really the principal axis, although as an axis of the first order only having a period of  $180^\circ$ , or  $120^\circ$  respectively, is at the same time an axis of the second order with characteristic angles of  $90^\circ$  and  $60^\circ$ .

And moreover it is also clear from these figures that in the case of *calcite* there is a real centre of symmetry, which on the contrary is absent in the case of *chalcopyrite*. The case of *Groeca pedalis*, as evidently belonging to the group  $D_8^D$ , we have drawn attention to before.<sup>1)</sup>

§ 11. The last groups which remain to be traced, are those which relate immediately to the three possible *endospherical* groups  $T$ ,  $K$ , and  $P$ , previously dealt with. Again we have to investigate what will be the result of their combination with  $S^H$ ,  $S^F$ ,  $S^D$ , and  $I$ .

In connection with our reasonings in the case of the analogous deductions from the group  $D_n$ , and bearing in mind that the groups  $T$  and  $K$  also possess among their characteristic operations a number of rotations round three binary axes which are perpendicular to each other, we may conclude in the same way as before that only the combinations with  $S^H$  and  $S^D$  will produce two *different* new groups in the case of  $T$ .

For  $S^H$  and  $S^D$  combined are equivalent to a rotation through  $180^\circ$  round an axis which bisects the angle between two of the above mentioned axes; this new binary axis is *not* present in  $T$ , but in  $K$  its direction is the line joining the middles of two opposite edges of the cube. Therefore the three new groups appear to be:  $T^H$ ,  $T^D$ ,  $K^H$ ; *other ones are not possible*.

With respect to the pentagonal dodecahedral group  $P$ , we find in quite the same way, that if the axial system of  $P$  should coincide with itself by the added operations of the second order, this addition can be executed only in such a way that the plane of reflection passes through two quinary, two ternary, and two binary axes at the same time. If one of the quinary axes is put in a vertical position, we can regard this added plane as  $S^F$ ; moreover it will bisect the angle of two pairs of other quinary axes, of two pairs

---

1) Of course the groups of the second order, which are related to  $D_n$  can be deduced as well from the groups  $\tilde{C}_n$  of the second order, by combining those with binary axes; just in the same way as in the previous chapter we have derived  $D_n$  from the cyclic groups  $C_n$ . This however may be left to the reader.

of binary axes, and of one pair of ternary axes, and therefore it has also some of the functions we have previously attributed to the "diagonal" planes  $S^D$ . On closer examination it appears also to be perpendicular to one of the binary axes of the system, and therefore it has in consequence the existence of a symmetry-centre.

Further it is obvious that it is impossible to add a horizontal plane  $S^H$ , perpendicular to the supposed vertical quinary axes; for this plane passing through five binary axes at the same time, does *not* bring the axial system of the group to coincidence with itself by a reflection in  $S^H$ . The final result is therefore that only  $S^V$ , — or what is in this case the same thing, — the *addition* of a *symmetry-centre* will produce a new group of the second order. We shall call it  $P^I$ , — with respect to this last mentioned way of deduction; the new group is thus derived by combining  $P$  with the inversion  $I$ .

Summing up, we thus find altogether *four* new groups of the second order, related to the endospherical groups  $T$ ,  $K$ , and  $P$ :

a. *There are symmetrical figures which have the axial system of the group  $T$ , three perpendicular planes of symmetry passing through every pair of binary axes, and a symmetry-centre. The ternary axes are at the same time senary ones of the second order. The symbol of this group shall be  $T^H$ .*

b. *There are symmetrical figures which possess the axial system of the group  $T$ , and six planes of symmetry passing through every pair of ternary axes. They have no centre of symmetry, but every binary axis is at the same time a quaternary one of the second order. We shall name this group  $T^D$ .*

c. *There are symmetrical figures which possess the axial system of the group  $K$ , three perpendicular planes of symmetry passing through every pair of quaternary axes, and six planes of symmetry passing through every pair of ternary axes. Moreover, they have a centre of symmetry. The ternary axes are at the same time senary ones of the second order. We shall denote this group by the symbol  $K^H$ .*

d. *There are symmetrical figures which have all axes of the group  $P$ , as well as fifteen planes of symmetry passing through two quinary, two ternary, and two binary axes simultaneously; moreover they have a centre of symmetry, and every axis of odd period is at the same time one of the second order with a period-number  $2n$ . We shall attribute the symbol  $P^I$  to this group. It represents the highest symmetry which*



a figure can possess if no axes with  $n = \infty$  are taken into account.<sup>1)</sup>

Finally we may draw attention to the fact that the group  $K^H$  contains all operations which are characteristic as well of the group  $T^H$  as of  $T^D$ . These last are therefore called *sub-groups* of  $K^H$ . In the same way the groups  $T$  and  $K$  themselves are *sub-groups* of  $K^H$ . Also in

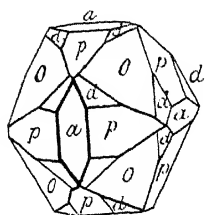


Fig. 82.  
*Pyrite.*

the case of the other symmetry-groups now deduced, we can indicate such sub-groups as contain a part of the operations of other, higher symmetrical combinations of symmetry-

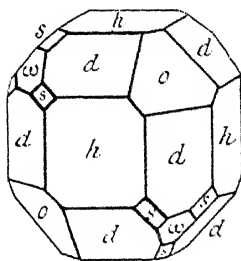


Fig. 83.  
*Boracite.*

elements. This fact is of importance, as we shall see afterwards, for the sake of combining several groups to larger ones, --- a process which is the basis of the division in crystal-systems and crystal-classes, as since early days it has been used in crystallography, and which simultaneously explains the deeper meaning of the old division of crystallographical polyhedra into *holohedral*, *hemihedral*, and *tetartohedral* forms, as was especially brought to the fore in Naumann's doctrine

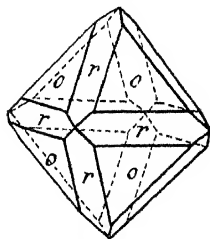


Fig. 84.  
*Fluorspar.*

§ 12. As illustrative examples of this symmetry, in fig. 82, 83, and 84, the crystal-forms of *pyrite*:  $\text{FeS}_2$  (fig. 82;  $T^H$ ), of *boracite*:  $\text{Mg}_7\text{B}_{10}\text{Cl}_2\text{O}_{30}$ , (fig. 83;  $T^D$ ), and of *fluorspar*:  $\text{CaF}_2$  (fig. 84;  $K^H$ ) are reproduced as some instances of the groups  $T^H$ ,  $T^D$ , and  $K^H$  respectively.

Of living beings, the pollen-cells of some plants may perhaps be mentioned here: thus of group  $T^H$  perhaps those of *Buchholzia maritima*; of  $T^D$  those of *Corydalis sempervirens*, and of group  $K^H$

<sup>1)</sup> Of course, if axes of isotropy are concerned too, the *spherical* symmetry is the highest possible one. Indeed, just in the same way as the sphere is an "endospherical" polyhedron with an infinite number of faces.

the pollen-cells of some *Polygoneae*, according to Haeckel's data.

However it is difficult to say whether such individuals belong really to this class, or only have the symmetry of the groups  $T$  and  $K$  themselves. If so, the drawings of fig. 49 may be included here, or the instances just mentioned may be among those given in the preceding chapter.

§ 13. *No other symmetry-groups than those deduced in the preceding are possible for finite stereometrical figures, as long as axes of isotropy are not concerned.* The whole investigation therefore has led to the result that the different types of symmetrical figures are only few in number, although of course their total number is infinitely great, because  $n$  can have all possible values.

If we review these principal types here once more, we shall find the following result:

A. *Symmetrical figures which differ from their mirror-images.*

1. Cyclic groups  $C_n$
2. Dihedron-groups:  $D_n$
3. Endospherical groups:  $T$ ,  $K$  and  $P$ .

All figures belonging to A may exist in two enantiomorphous forms.

B. *Symmetrical figures, which are identical with their mirror-images.*

4. Cyclic groups of the second order:  $\overline{C}_n$ ; special cases:  $S$  and  $I$ .
5. The groups:  $C_n^V$  and  $C_n^H$ .
6. The groups:  $D_n^H$  and  $D_n^D$ .
7. The groups:  $T^H$ ,  $T^D$ ,  $K^H$ , and  $P^I$ .

The number of these different types does not exceed fourteen or sixteen; for finite figures this exhausts the possible symmetries if  $n$  gets all values from 1 to infinitely great. The groups with axes of isotropy ( $n = \infty$ ) will be dealt with in detail in the following chapter.

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## CHAPTER V.

The Limits of the axial periods in Crystalline Matter. — Haüy's Law. — Crystallographically occurring Symmetry-Axes. — Groups and Sub-groups; their relation to Holohedral, Hemihedral and Tetartohedral Crystal-Classes. — Crystal-systems. — Gadolin's Projection of Symmetry-Elements. — The Symmetry-Classes of the Cubic System. — General and special simple Forms. — Symmetry-groups with Axes of Isotropy. — The Symmetry of a Physical Phenomenon, of a Physical State, and of a Physical Medium. — The "image" of a Physical Phenomenon. — The Symmetry of Cause and Effect, and their mutual Relation. — The Symmetry of the Electrostatic and that of the Magnetic Field. — The Symmetry of centrally-symmetrical Phenomena in Crystals. — The Superposition of Different Causes. — Symmetry and Dissymmetry. — General Remarks on the symmetrical Arrangement of experimentally determined Numbers. — Problems and Investigations of the Future. —

§ 1. In the preceding chapters we extended our researches to include all kinds of symmetrical systems. It need hardly be remarked that, as evidently no special circumstances prohibit the occurrence of every kind of symmetry-axes in the objects of living nature, such a general way of treating the problem was the indicated and only effectual one for the application of the doctrine of symmetry in the whole domain of natural science. However in the case of other, non-living natural objects, experience teaches us that by no means such an unlimited variety in the periods of the symmetry-axes manifests itself; and more particularly in the domain of *crystalline* matter, there must be some reason why certain limits are apparently set to the possible values of the numbers  $n$ , and to the characteristic periods of the symmetry-axes, as these are determined by  $n$ .

Indeed, in no field of physical research does the significance of

the symmetry-principle come so strongly to the fore, as where crystalline matter is considered: even in early times the typical polyhedral forms of the crystals and their beautiful geometrical shapes made so strong an impression on observers, that for a long while this external form was considered the *essential* feature of the crystalline state in general.

Thus crystallographical research was developed primarily by the intense and exclusive study of the polyhedral limiting forms of the crystals; and it was by investigations of this kind that Haüy more than a hundred years ago discovered the fundamental law which

bears his name, and which gives the key to the remarkable fact above mentioned, that only symmetry-axes with a rather small number of quite determined periods are met with in such crystal-polyhedra.

§ 2. The law of Haüy, which became the very foundation of modern crystallography, may be elucidated as follows.

Let  $XOY$ ,  $XOZ$ , and  $ZOY$  (fig. 85) be three arbitrary faces of a crystal, of which faces the intersections are not parallel to the same straight line in space; their edges  $OX$ ,  $OY$ , and  $OZ$  intersect in  $O$ . Let  $ABC$  be another face of the crystal. The segments

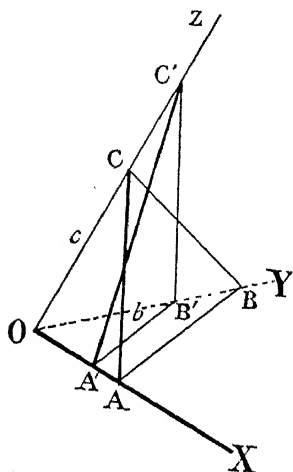


Fig. 85.

$a$ ,  $b$ , and  $c$ , cut off by this plane  $ABC$  on the axes  $OX$ ,  $OY$ , and  $OZ$  chosen as coordinate-axes, shall fix its position entirely. Now according to the law discovered by Haüy, any other possible face of the crystal, — let us say  $A'B'C'$ , — must necessarily fulfil the special condition that the ratio of the segments  $OA' : OB' : OC'$  be always expressible in the form:  $ma : nb : pc$ , the numbers  $m$ ,  $n$ , and  $p$  being rational numbers, and in most cases even very simple ones.

These numbers  $m$ ,  $n$ , and  $p$  are quite sufficient to fix the plane  $A'B'C'$  with respect to its direction in space, as determined by the perpendicular from  $O$  upon it; and thus, if  $OA'$  be taken equal to  $ma$ ,  $OB'$  and  $OC'$  will assume the values  $nb$  and  $pc$  at the same time. In crystallography these numbers  $m$ ,  $n$ , and  $p$  themselves are not

commonly used in calculations, but rather their *reciprocal* values:  $h = \frac{1}{m}$ ,  $k = \frac{1}{n}$ , and  $l = \frac{1}{p}$ . These numbers  $h$ ,  $k$ , and  $l$  are called the *indices* of the crystal-face (Miller), and the plane itself is usually denoted by the symbol  $(h\ k\ l)$ . As only the *ratio*:  $ma: nb: pc$ , is of interest for the determination of the *direction* of  $A'B'C'$ , these numbers  $h$ ,  $k$ , and  $l$  are generally reduced to the most simple integers.

The law of Haüy may therefore be expressed as follows:

*Only such faces can occur as limiting faces of a crystal, the indices of which are (simple) rational numbers, if these faces are defined with respect to four not parallel and suitably chosen planes of the crystal.*<sup>1)</sup>

§ 3. It is this very important law which determines the limits, within which the possible values of the periods of eventually occurring symmetry-axes in the crystal must remain. These limits may be fixed in two ways: either we can look upon the external form of the crystal only, or we can try to explain Haüy's law by some suitable hypothesis on the molecular structure of the crystal, and see if this supposed structural image possess a special character from which the limits of the axial periods mentioned above follow as a logical consequence. Indeed, Haüy's law has led to such suppositions about the intimate, molecular structure of crystals in general, — a theory which has been of great value in the development of our views on the true nature of crystalline matter. These views have been strikingly confirmed by the results lately obtained in the recent experiments of Von Laue, Bragg Sr. and Jr., and others, who sent a narrow pencil of Röntgen-rays through a crystal, and obtained in such a way a diffraction-pattern which is closely related to the said molecular structure. Although the fundamental correctness of the above mentioned ideas regarding the molecular structure of the crystals has thereby become highly probable, it is however better to postpone the demonstration based upon these views till we are dealing in detail with the indicated systems of molecules regularly distributed in space. With respect to our previous

1) Although the condition of *simplicity* of the indices considered is not an essential one, it may be clear that in *practice* the law of Haüy can be of value only if these numbers be really simple ones too. For the ratio of the intercepted segments on the coordinate-axes, with respect to those of the primarily chosen fourth plane, can be *always* reduced to a set of *rational* numbers, if only we are free to multiply the observed ratio by any suitably chosen factor, *whatever may be the magnitude of the last*.

investigations it is perhaps preferable to give a simple demonstration now, in which only the properties of the external, polyhedral form of the crystals are made use of; we think this demonstration for

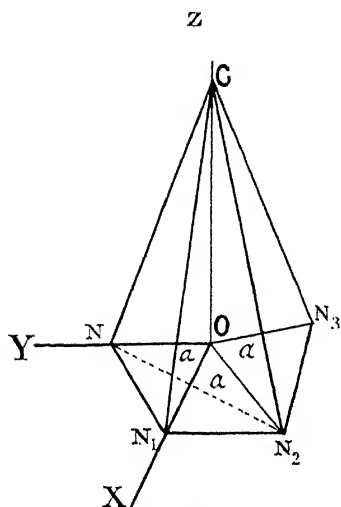


Fig. 86.

the present purpose will be sufficiently clear.<sup>1)</sup>

Let  $ZO$  in *fig. 86* be a symmetry-axis of the first order, with a characteristic angle  $\alpha = \frac{2\pi}{n}$ ;  $ON$  is a possible<sup>2)</sup> crystal-edge, situated in the plane  $XOY$  perpendicular to  $ZO$ .

By rotations round  $ZO$  through angles  $\alpha, 2\alpha, 3\alpha$ , etc.,  $ON$  is repeated  $n$  times. Because all edges  $ON$  may be used as coordinate-axes, we shall here take  $OZ$ ,  $ON$ , and  $ON_1$ , as  $Z$ -,  $Y$ -, and  $X$ -axis respectively. If now  $CNN_1$  be a possible crystal-face<sup>3)</sup>, then of course the same will be true

for  $CN_1N_2$ ,  $CN_2N_3$ , etc., and the mutual intersections of all these planes, e.g.  $NC$ ,  $N_1C$ ,  $N_2C$ , etc., will be crystallographically possible edges too. But if so, such planes as  $NCN_2$ , intersecting  $ON_1$  in  $S$ , must be possible crystal-planes, because they pass through two intersecting possible edges of the crystal. Therefore the plane  $NCN_2$

<sup>1)</sup> A. Gadolin, *Acta Soc. Scient. Fenn.* (1871), § 3; *Ostw. Klass. d. ex. Wiss.* No. 75, p. 7, 74—83. (1896).

<sup>2)</sup> The intersections of possible (i.e. possible in the sense of Haüy's law) crystal planes are always possible crystal-edges. Cf. the demonstration in: A. Gadolin, *Ostw. Klass.* No. 75, p. 74—78. As a corollary it follows that every plane passing through two non-parallel possible edges of a crystal, is a possible crystal-plane too.

<sup>3)</sup> If  $CNN_1$  is not a possible plane, but e.g.  $CNn_1$ ,  $On_1$ , being  $\geq ON_1$ , the successive intersections  $Nn_1$ ,  $N_1n_2$ ,  $N_2n_3$ , etc., in plane  $XOY$  will not form a closed polygon, if the lines  $Nn_1$ ,  $N_1n_2$ , etc., be not continued until they intersect in points  $s_1$ ,  $s_2$ , etc. The lines joining  $C$  with  $s_1$ ,  $s_2$ , etc., are now the intersections of a regular pyramid of  $n$  sides, and a figure analogous to the one above, may now be used also for the purpose of demonstration. This last one can therefore be considered to be sufficiently general.

must cut off segments of such magnitude on the three coordinate-axes  $OZ$ ,  $ON$ , and  $ON_1$ , that Hauy's law shall be fulfilled: thus in the case considered the proportion  $\frac{OS}{ON_1}$  must be a rational one. But  $\frac{OS}{ON_1}$  being equal to  $\frac{OS}{ON}$ , — because  $NS$  is perpendicular to  $ON_1$ , — is none other than  $\cos \alpha$ . Therefore if Hauy's law will hold,  $\cos \alpha$  must have a *rational* value, and the only allowable values of this kind are:  $0$ ,  $+\frac{1}{2}$  or  $-\frac{1}{2}$ , and  $+1$  or  $-1$ , the angle  $\alpha$  being then  $90^\circ$ ,  $60^\circ$ ,  $120^\circ$ ,  $0^\circ$ , and  $180^\circ$  respectively <sup>1)</sup>. From this it follows that in crystallographical polyhedra no other symmetry-axes can occur than those which are characterised by the values 1, 2, 3, 4, and 6 for  $n$ . All other values of  $n$  are excluded in the case of crystals, because the validity of Hauy's law requires this. Hence we may conclude:

*The symmetry-axes of crystallographical polyhedra can only be binary, ternary, quaternary, and senary axes* <sup>2)</sup>).

§ 4. The number of crystallographically possible symmetry-groups, as deduced from the complete number of types already traced by us, therefore proves to be limited to *thirty-two*. Their symbols are, in the same order as the general groups found previously, the following <sup>3)</sup>:

A. *Groups of the first order:*

$C_1$ ,  $C_2$ ,  $C_3$ ,  $C_4$ ,  $C_6$ ;  $D_2$ ,  $D_3$ ,  $D_4$ ,  $D_6$ ;  $T$ , and  $K$ .

All crystals appearing in two enantiomorphous forms belong to one of these eleven classes.

B. *Groups of the second order:*

$C_1$ ,  $C_2$ ,  $C_4$ ;  $C_2^H$ ,  $C_3^H$ ,  $C_4^H$ ,  $C_6^H$ ,  $C_2^V$ ,  $C_3^V$ ,  $C_4^V$ ,  $C_6^V$ ;  $C_3^I$ ;  
 $D_2^H$ ,  $D_3^H$ ,  $D_4^H$ ,  $D_6^H$ ;  $D_2^D$ ,  $D_3^D$ ;  $T^H$ ,  $K^H$ ;  $T^D$ .

All crystals which do *not* differ from their mirror-images, belong to one of these twenty-one classes.

N. B. Attention must be drawn *again* to the fact so often misunderstood, that the absence of a plane of symmetry need *not* necessarily make the figure considered differ from its mirror-image. The reverse of this.

<sup>1)</sup> For the complete demonstration, vid. N. Boudajef, in Ostw. Klass. No. 75, p. 78—83. (1896).

<sup>2)</sup> In crystallography these axes are usually named: *digonal*, *trigonal*, *tetragonal* and *hexagonal* axes, with respect to the polygonal and polyhedral forms occurring.

<sup>3)</sup> The case of  $n = 1$  ( $\alpha = 2\pi$ ) has been also considered here, although the axis  $A_1$  has, properly speaking, significance only as a symbol for *identity*. The groups with such "unary" axes will therefore afterwards be indicated by the special symbols  $A$  and  $S$  respectively.



is certainly true, as well as the other view, according to which enantiomorphous figures have *never* a symmetry-centre. The above mentioned thesis however is *not* correct, as has been clearly shown in the preceding chapters. Stereometrical figures are different from their mirror-images, and they can therefore occur in two non-superposable forms, — only when they do *not* possess *any symmetry-properties of the second order*, whatever they may be. Neither the absence of a symmetry-centre, nor that of a symmetry-plane is therefore sufficient to have enantiomorphism as a necessary consequence. This fact already repeatedly mentioned in the preceding chapters, should be kept in mind, especially by authors on chemical subjects, writing about molecular symmetry; in many textbooks on organic chemistry these relations are wrongly treated. We shall have occasion to return to this subject later on, more especially when we come to deal with Pasteur's law.

The thirty-two symmetry-groups mentioned can now readily be arranged in a more systematic way if we remember the formerly indicated relations existing between mathematical "groups" and "sub-groups" (p. 72). We have seen that if a number of non-equivalent operations out of a group of them, be taken so that they may be combined to form a new complete group of operations, this new group is called a *sub-group* of the original one. The number of non-equivalent operations of a sub-group is always an aliquot part of the number of operations present in the original group.

Thus, for instance, the group  $K$  contains all operations of the group  $T$  (p. 72), and therefore  $T$  is a sub-group of  $K$ . Now while  $K$  includes *twenty-four non-equivalent operations of the first order*,  $T$  has just *half* that number, i. e. *twelve*; etc.

In crystallography it is usual to reunite all sub-groups  $g_1$ ,  $g_2$ ,  $g_3$ , etc., of another higher symmetrical group  $G_0$ , with that group  $G_0$ , and form them together into one and the same *crystal-system*.

Because of the fact that the number of non-equivalent operations of these sub-groups is always an aliquot part of that of the principal group, and that therefore this is also the case with the number of the limiting faces of the crystals, if they are bordered by the most unrestricted simple form of every class, — these sub-groups are distinguished from the principal one, by the names *hemihedral* and *tetartohedral* groups respectively, while the principal group itself is called the *holohedral* group.

This gathering of the sub-groups with their principal one into a *crystal-system*, has many practical advantages. One of the most important being that all crystal-forms belonging to the same crystal-system, can be described with respect to *the same set of coordinate-*

axes, whether their symmetry be a higher or a lower one. As a consequence of this, the parameters of the forms of all classes belonging to the same crystal-system, are fully determined by *the same number of independent measurements*: the higher the special symmetry of the lowest-symmetrical sub-groups of the system is, the smaller is the number of such independent data required for the determination of the coordinate-system and the parameters of a crystal.

If now we investigate, which groups of the thirty-two mentioned above are sub-groups of others, we get the following *seven* crystal-systems. The principal group in every system, of which the others are sub-groups, is always mentioned as the first one:

- I. The *triclinic system* includes the groups:  $I$  and  $A$  ( $= C_1$ ).  
The polyhedra of every class of this system can be absolutely fixed by *five* independent data <sup>1)</sup>.
- II. The *monoclinic system* includes the groups:  $C_2^H$ ,  $S$ , and  $C_2$ .  
The forms of this system are fully determined when *three* independent data are given.
- III. The *rhombic system* includes the groups  $D_2^H$ ,  $C_2^V$ , and  $D_2$ .  
All forms of the whole system are known if *two* independent data are given.
- IV. The *tetragonal system* includes the groups:  $D_4^H$ ,  $D_2^D$ ,  $C_4^H$ ,  $C_4^V$ ,  $\bar{C}_4$ ,  $D_4$ , and  $C_4$ .  
All polyhedra of this system are determined by *one* single measurement.
- V. The *trigonal system* includes the groups:  $D_3^H$ ,  $D_3^D$ ,  $C_3^H$ ,  $C_3^V$ , and  $D_3$ ,  $C_3^I$ , and  $C_3$ .
- VI. The *hexagonal system* includes the groups:  $D_6^H$ ,  $D_6$ ,  $C_6^H$ ,  $C_6^V$  and  $C_6$ .

<sup>1)</sup> Three independent data are generally sufficient to fix a coordinate-system, whether there be given three angles between every pair of coordinate-axes, or the three dihedral angles between every pair of coordinate-planes, or any arbitrary combination of three such elements. For the determination of a fourth plane of the crystal, *two* other data are necessary and sufficient. But if this plane be determined, all other planes of the crystal follow from it according to Haüy's law. If now the coordinate-system is not arbitrary, but a higher symmetrical one, whose angles have fixed and known values ( $90^\circ$ ,  $60^\circ$ ,  $45^\circ$ , etc.), then of course the number of data required to define it, is reduced more and more, while the same will be the case with respect to the fixing of the fundamental fourth crystal-plane mentioned before.

All polyhedra of both the trigonal and hexagonal system are determined by *one* single measurement, just as was the case in the tetragonal system.

- VII. The *cubic system* includes the groups:  $K^H$ ,  $T^H$ ,  $T^D$ ,  $K$ , and  $T$ .

In this system *no* measurement is required to characterise any form completely: all forms have special and invariable values of their dihedral angles.

From this it is obvious that quite independently of the introduction of conceptions such as: *hemihedrisms*, *tetartohedrisms*, *holohedrisms*, etc., into the science of crystallonomy, a grouping such as above explained, presents itself as a very natural one, in so far as such groups *which have all certain characteristic properties in common*, are gathered into one and the same greater unit. Thus e.g., all groups  $K^H$ ,  $T^H$ ,  $T^D$ ,  $K$ , and  $T$ , have four ternary axes in common; the groups:  $D_6^H$ ,  $D_6$ ,  $C_6^H$ ,  $C_6^V$  and  $C_6$  possess all a *single senary axis*, etc. It is upon this basis that the arrangement in "crystal-systems" is really founded; and the deduction of the lower symmetrical forms of each system from the higher ones by partial suppression of their faces appears to be artificial and unnecessary.

§ 5. An easy and clear review of all symmetry-properties, as well as of the most unrestricted forms of each class, may now be obtained in connection with the above stated facts, if a way of representing axes, planes of symmetry, and crystal-faces be made use of, which takes its origin also from Gadolin.<sup>1)</sup>

This author uses for that purpose a special form of the so-called "stereographical projection" in which the axes, planes of symmetry, and faces of the polyhedral object are represented in a simple way; and this method may also be made use of in cases where the determination of the real symmetry of a given form in nature is required, e. g. in morphological work. Some short remarks upon this method in general, seems therefore to be in place here.

A stereographical projection of a crystal for instance, is obtained, if from some point in space  $O$  perpendiculars are drawn upon all faces of a crystal (*fig. 87*), and if these perpendiculars are continued to their intersection with a spherical surface, described with a radius  $R$  round the point  $O$  as a centre. If now the diametrical plane  $VV'$  e. g., be chosen as the plane of projection, the projections of

<sup>1)</sup> A. Gadolin, loc. cit.; Ostw. Klass. No. 75, p. 32. (1896).

all points  $P$  will be obtained by joining them to a point  $M$  opposite to  $N$ , which is called the *pole* of the projection, and if the intersections  $S$  of  $V$  with the straight lines  $MP$  are considered. All points  $S$  thus obtained, form together the *stereographical projection* of the crystal  $F$ .<sup>1)</sup>

Now Gadolin determines the direction of the symmetry-axes and of the perpendiculars to the crystal-faces just in the same way. Only he superposes the two images which would be obtained by projection of the upper and the lower half of the polyhedron, if observed from  $M$  or

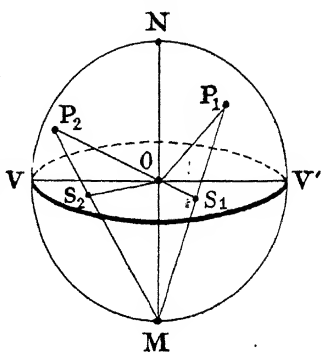


Fig. 87.

from  $N$  respectively, and he distinguishes the faces above and beneath the plane of projection  $V$  simply by different signs, e. g. by  $\times$  and  $\circ$ . The period of the axes is denoted in the way described further on.

For the purpose of illustrating the application of this method for the representation or the eventual determination of the specific symmetry of a body or of its general form, we will apply it in the case of the *cubic system* only, and deduce in this way the most unrestricted polyhedral forms in every class of it. It will then be easy in the same way to extend such considerations to every other class of crystals.

Moreover it may be mentioned that the method indicated here may be recommended in all cases where the special symmetry of some complicated form or object has to be found. Thus the special symmetry of many complicatedly built *radiolaries*, e. g. of *Etmospaera siphonophora* (Haeckel), etc., or the arrangement of their *spicula*, or the type of symmetry of a flower or of some animal, may often easily be found, if the repeatedly occurring parts of the object be projected in the way considered, upon a spherical surface, and

<sup>1)</sup> For the full application of the stereographical projection and its properties, we may refer here to the numerous treatises on crystallography, in which this method is explained in detail. Cf. more particularly: H. E. Boeke, *Die Anwendung der stereographischen Projektion bei krystallographischen Untersuchungen*, Berlin, (1911).

every projected part be denoted by a special sign. Even in rather complicated cases the real symmetry can thus generally be found without much difficulty.

§ 6. If now we review the special symmetry of the *five classes of the cubic system* in the way of Gadolin, we obtain the following images.<sup>1)</sup>

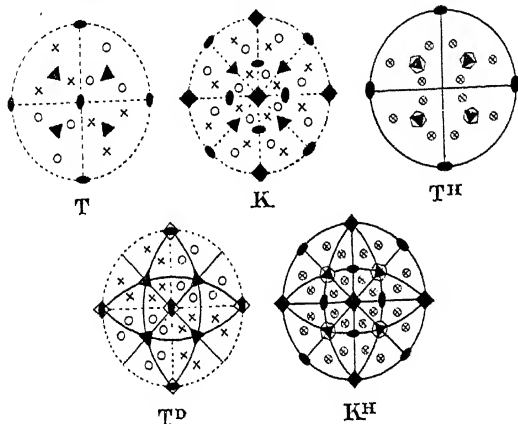


Fig. 88.

Stereographical Projection of the Groups of the Cubic System.

The most unrestricted forms of any of these five classes are reproduced in *fig. 89*.

They have successively twelve, twenty-four, and forty-eight limiting faces, and are usually called *tetrahedral-*

*pentagonal-dodecahedron*, *pentagonal-icositetrahedron* (gyroid), *dyakis-dodecahedron* (didodecahedron; diploid), *hextetrahedron*, and *hexoctahedron* respectively, and their general Millerian symbol is  $\{hkl\}$ .

In the cubic system the three planes passing through every pair of the perpendicular binary or quaternary axes, parallel to the edges of a cube, are always taken as coordinate-axes. If now the stereographical projection of a limiting face of the form considered, should happen to coincide with the point of intersection of the sphere

<sup>1)</sup> As already stated, the faces on the upper half of the sphere are indicated by  $\times$ , on the lower half by  $\circ$ . A binary axis bears an ellipsoid  $\bullet$ , a ternary one a triangle  $\blacktriangle$ , etc. at its ends. An axis of the second order is indicated by an *open* polygon:  $\bigcirc$ . The axes are represented by *dotted* lines; if they are situated *in a plane of symmetry*, by a *continuous* line. If the circle in the plane of projection is a *continuous* curve, it means that this plane of projection is also a plane of symmetry; etc. These notations are now commonly adopted, especially among German crystallographers. The above reproduced figures will now be easily understood.

with one of the coordinate-axes, or if it be situated in one of the coordinate-planes, etc., or if that face be parallel to a coordinate-axis or to a coordinate-plane, then the symmetrical repetition of that face will determine a simple form of each crystal-class, which does no longer agree with the most unrestricted, general form of that class. These new simple forms, on the contrary, will possess *less* limiting faces than the most unrestricted one, and therefore will have a simpler shape and a simpler Millerian symbol. In the next table a review is given of the special cases mentioned for every class of the regular system, and the corresponding Millerian indices for every form are there indicated also.

TABLE OF THE PRINCIPAL FORMS OF THE CUBIC SYSTEM.					
Symmetry:	Group <i>T</i> :	Group <i>K</i> :	Group <i>TH</i> :	Group <i>TD</i> :	Group <i>KH</i> :
Miller's symbol:	pos. and neg. <i>d</i> and <i>l.</i> tetrahedral Pentagonal dodecahedron.	<i>d</i> and <i>l.</i> Pentagonal-icositetrahedron. (Gyroid).	<i>d</i> and <i>l.</i> Dydodecahedron. (Didodecahedron; Diploid).	pos. and neg. Hextetrahedron.	Hexoctahedron.
$\{hkl\}$	pos. and neg. Deltoiddodecahedron.	Trisectahedron.	Trisectahedron.	pos. and neg. Deltoiddodecahedron.	Trisectahedron.
$\{hkk\}$	pos. and neg. Tristetrahedron.	Icositetrahedron.	Icositetrahedron.	pos. and neg. Tristetrahedron.	Icositetrahedron.
$\{hko\}$	pos. and neg. Pentagonal dodecahedron.	Tetrahexahedron.	<i>d</i> and <i>l.</i> Pentagonal dodecahedron.	Tetrahexahedron.	Tetrahexahedron.
$\{III\}$	pos. and neg. Tetrahedron.	Octahedron.	Octahedron.	pos. and neg. Tetrahedron.	Octahedron.
$\{IIO\}$	Rhombicdodecahedron.	Rhombicdodecahedron.	Rhombicdodecahedron.	Rhombicdodecahedron.	Rhombicdodecahedron.
$\{IOO\}$	Cube.	Cube.	Cube.	Cube.	Cube.

The *constant* forms, occurring in all classes of the system, are: the *cube*  $\{IOO\}$ , and the *rhombicdodecahedron*  $\{IIO\}$ , the *octahedron*  $\{III\}$  eventually being split up into a positive and a negative *tetrahedron*.

Besides the general forms  $\{hkl\}$ , in the *fig. 90*, the whole series of simple forms which occur for determined values of *h* and *k*, are reproduced here; the crystals in nature are of course generally more or less complicated combinations of several of these simple forms occurring at the same time, and usually with very different relative development of the existent forms.

That gradual transitions between these forms can be imagined with variation of the values of  $h$ ,  $k$ , and  $l$  from zero to every arbitrary integer number, is obvious on comparing the different simple forms with each other.

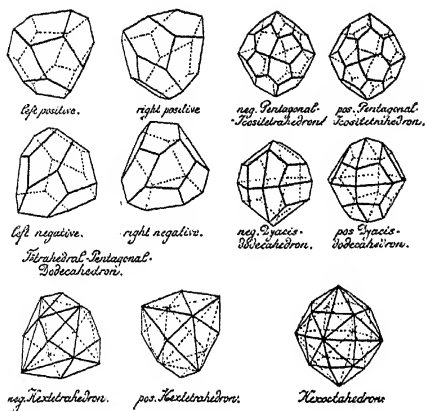


Fig. 89.

application of this principle to the other possible classes we shall arrive at all possible simple forms of crystals, and thus the consequent development of these ideas is best left to treatises on crystallography, as this book deals with general aspects of the subject only, rather than with its applications to a special science<sup>1)</sup>.

§ 7. We therefore prefer to draw attention to some other subjects relating not only to the symmetry of crystalline matter, but to that of physi-

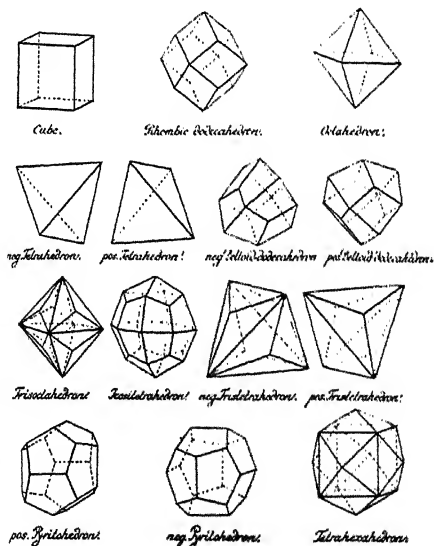


Fig. 90.

<sup>1)</sup> It may be remarked that the same views hold in the case where not

cal phenomena and physical states in the broadest sense of the word. Also in these questions we shall in most cases not go into minute details of such phenomena, but content ourselves with indicating the general way of deduction and only occasionally shall we give some special illustrations of what is said, by considering some striking phenomena more in particular.

In this connection we must remember in the first place, that for us those cases are of special interest, in which the axis, or the axes of symmetry, have a period which is *infinitely small*,  $n$  in the expression:  $\alpha = \frac{2\pi}{n}$  being *infinitely great*. We have called axes of this kind, *axes of isotropy*; and there are many physical phenomena in which they play a preponderant rôle. The possible symmetries in systems which possess such axes of isotropy, are easily deduced if the corresponding groups of symmetry be considered as the limiting cases to which the endospherical-groups, the dihedron-groups  $D_n$ , and the cyclic groups  $C_n$ , — both of the first and of the second order, are approaching, when the number  $n$  gradually increases.

On closer examination all endospherical groups appear to approach then to two definite groups, which will be called *spherical groups*, and to which we shall attribute the symbols  $K_\infty^H$  and  $K_\infty$  respectively.

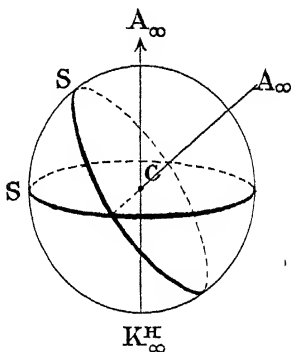


Fig. 91.

the crystal forms, but the so-called „solution-bodies” are investigated. In general these approximately polyhedral objects, limited by curved planes, and obtained by the slow action of a solvent on a sphere cut from a homogeneous crystal, are the *polar-forms* of the crystal-forms. Therefore they possess also the same symmetry as these have. The solution-phenomena mentioned were first studied by Lavizzari, and more in detail, with success by Goldschmidt and others Cf. also: L. Lavizzari, *Nouv. Phénomènes des Corps cristallisés*, Lugano, 1865; V. Spring, *Zeits. f. phys. Chemie*, **2**. 13. (1888); G. Cesarò, *Ann. de Chim. et Phys.* **17**. 37. (1889); V. Goldschmidt and F. Wright, *Neues Jahrb. f. Miner.* (1903); *Beil. Bd.* **18**. 235. (1904); **26**. 151. (1908); *Zeits. f. Kryst.* **38**. 656. (1904); **50**. 459. (1912); O. Mügge, *Festschr. H. Rosenbusch*, (1906). p. 96; A. Johnsen, *82e Vers. Deuts. Naturf. und Aerzte, Königsberg*, (1910); W. Burkhardt, *Inaug. Diss., Leipzig*. (1911); W. Schnorr, *Zeits. f. Kryst.* **54**. 289. (1914); etc.



The group  $K_{\infty}^H$  is characterised by the possession of an infinite number of axes of isotropy, by that of an infinite number of symmetry-planes, and by the presence of a symmetry-centre.

The symmetry of the group  $K_{\infty}$  consists in the presence of an infinite number of axes of isotropy, but it does not possess any symmetry-planes, nor a centre of symmetry.

The symmetry of the group  $K_{\infty}^H$  is the highest symmetry which can eventually be attributed to a system. Each arrangement of an infinite number of points deprived of all qualities, or which are at least deprived of all "directional" properties, represents a system having this symmetry; and even if directional qualities of a certain kind are present, but the points are distributed in space in such a way that no preference whatever for any direction is manifested, — the directional qualities thus becoming effaced by this, — the system as a whole will yet have the symmetry  $K_{\infty}^H$ .

If however this effacing influence of the distribution in space is *not* present, then the occurrence of such "directional" qualities will have as a necessary consequence that the symmetry of the system becomes a lower one than that represented by the group  $K_{\infty}^H$ .

Thus, if the physical state of every molecule of an optically active liquid be represented by a small portion of a screw-thread, a sphere filled with such a liquid can be considered as an object having the symmetry of the group  $K_{\infty}$ , — an infinite number of axes of isotropy still being present, but no planes of symmetry, nor a symmetry-centre.

Furthermore there are *five* other groups possible which possess a *single axis of isotropy*  $A_{\infty}$ ; in connection with their intimate relations to the dihedron- and cyclic groups of the first and second order, we shall denote them by the symbols:  $D_{\infty}^H$ ,  $C_{\infty}^H$ ,  $D_{\infty}$ ,  $C_{\infty}^V$ , and  $C_{\infty}$  respectively.

The group  $D_{\infty}^H$  has a *single homopolar axis of isotropy*  $A_{\infty}$ , a *plane of symmetry perpendicular to it*, an *infinite number of symmetry-planes passing through*  $A_{\infty}$ , and a *centre of symmetry*.

A cylindrical flask filled with a hypothetical, homogeneous, and weightless liquid, may be mentioned as an instance of a system having the symmetry  $D_{\infty}^H$ .

The group  $C_{\infty}^H$  possesses: a *homopolar axis of isotropy*  $A_{\infty}$ , a *plane of symmetry perpendicular to it*, and a *symmetry-centre*, but *no planes of symmetry passing through*  $A_{\infty}$ .

If a cylinder with circular base be rotated round its axis in a

definite direction with a constant angular velocity, the body as a whole may be said to have the symmetry of the group  $C_{\infty}^H$ . Indeed, if the rotating cylinder be reflected in a plane perpendicular to its axis of revolution, the mirror-image is congruent with the cylinder itself, while the image changes in no way by a rotation through an angle of  $180^\circ$  round an axis perpendicular to the reflecting plane.

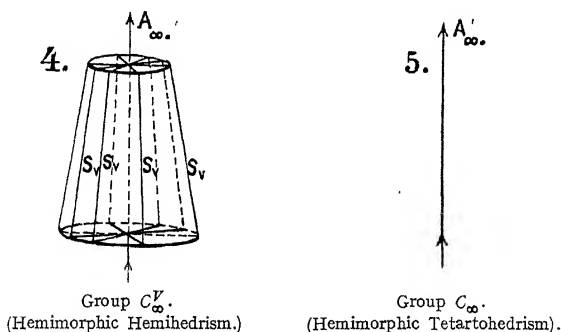
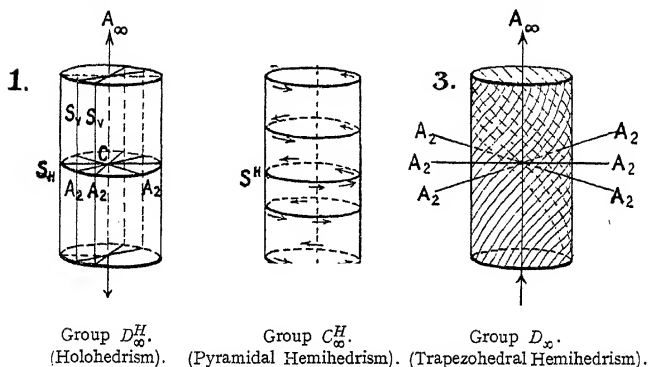


Fig. 92.

*Symmetry-Groups with a single Axis of Isotropy.*

And because the two operations mentioned are together equivalent to an inversion, the rotating cylinder is evidently congruent with its inverse image, which means that it has itself an inversion-centre.

The group  $D_{\infty}$  possesses a single homopolar axis of isotropy  $A_{\infty}$ , and an infinite number of binary axes perpendicular to it.

As the group  $D_{\infty}$  does not possess a symmetry-centre (just as in the case of  $D_n$ ), the symmetry can be also described by considering

$A_\infty$  as a screw-axis of infinitely small period, with an infinitely small corresponding translation in the direction of the axis. The binary axes mentioned are thus arranged like the infinitely low steps of a spiral-staircase, be it dextro- or laevogyratory. There are no planes of symmetry, nor a symmetry-centre present. If a cylindrical rod be twisted by two equal but oppositely directed couples at each of its ends, the whole system can be reckoned to have this symmetry  $D_\infty$ .

The group  $C_\infty^V$  has a heteropolar axis of isotropy  $A_\infty$ , and an infinitely great number of symmetry-planes passing through it.

It has neither binary axes, nor a symmetry-centre.

A truncated circular cone may be mentioned as an object having this symmetry. Every vector which represents a force, a velocity, etc., possesses the same symmetry; and it can be attributed also to the electric current, or to the homogeneous electrostatic field of force.

Finally the group  $C_\infty$  has no other symmetry-elements than a single heteropolar axis of isotropy  $A_\infty$ .

An upright circular cone which is rotated round its axis with a constant angular velocity in a definite sense, is an instance of an object having this symmetry. In *fig. 92* some schematical figures will elucidate what is said here in the above.

§ 8. Although the five groups mentioned now possess, properly speaking, an *infinitely great* number of non-equivalent symmetry-properties, it can be easily understood however that the groups  $C_\infty^H$ ,  $C_\infty^V$ , and  $D_\infty$  only possess *half*, and  $C_\infty$  even no more than a *quarter* of the symmetrical operations which are characteristic of  $D_\infty^H$ . They are related therefore to the last mentioned groups as "sub-groups" are with respect to their "principal group", — just in the same way as *hemihedral* and *tetartohedral* crystal-classes are related to their *holohedral* class of the same crystal-system. Indeed, if by analogy,  $D_\infty^H$  be considered as the holohedral class of the "isotropic" system,  $C_\infty^H$  will represent the "pyramidal",  $D_\infty$  the "trapezohedral" and  $C_\infty^V$  the "hemimorphic" hemihedrism of that system, while  $C_\infty$  may be considered to be a "tetartohedral" class of it. P. Curie pointed already to this analogy of the groups considered with those of the ordinary crystal-systems.<sup>1)</sup>

§ 9. Now we must draw closer attention to the question: how

<sup>1)</sup> P. Curie, Bull. de la Soc. Miner. 7. 418, a. f. (1884).

is it possible to speak of the "specific symmetry" of a physical phenomenon, of a physical state, or of a physical medium?

As long as an unlimited system is considered, built up by a very great number of points deprived of all special qualities, such a system as a whole can only possess the symmetry of the group  $K_{\infty}^H$ .

But if every point  $P$  of the system under investigation has itself *vectorial* properties, defined by *magnitude and direction*, the system shall have the lower symmetry of one of the groups  $D_{\infty}^H$ ,  $C_{\infty}^H$ ,  $C_{\infty}^V$ ,  $D_{\infty}$ , or  $C_{\infty}$ , — namely as long as the previously mentioned condition is fulfilled, that the distribution of the points in space does not show a lack of preference for some particular direction, because in that case the vectorial qualities would become effaced in the whole. As long as in  $P$  or in its immediate environment only *scalar* properties (temperature, density, etc.) are concerned, which are functions of the coordinates of  $P$ , the symmetry of the system will also be no other than that of the group  $K_{\infty}^H$ .

For determining the physical state in every point  $P$  of such a system, it is necessary to consider an infinitely small volume-element in the immediate vicinity of  $P$ . Such a volume-element can have a certain symmetry; the parameters by which its momentary state is characterised, can be the same or different in the various points  $P$ ,  $P'$ ,  $P''$ , etc. of the system, according as the system is a homogeneous or an inhomogeneous one.

Now the vectorial qualities in a volume-element round every point  $P$  can in most cases be represented by a certain suitable figure  $f$ , which we shall call the "image" of the physical state in  $P$ . We can consider in this way the "image" of a single molecule, or of a group of molecules, or of a volume-element yet containing a very great number of such molecules, — which in this last case however are *not* considered in it *separately*. Finally it may be desirable to consider the symmetry of a system or of a body as a whole. But the "image"  $f$  must always be chosen in such a way that it really describes the physical state to be investigated, *as completely as possible*, and often it is by no means an easy matter to find out the suitable form of  $f$  for this purpose. If this really be the case, the figure  $f$  must be of such a nature that, if in  $P$  three coordinate-axes  $OX$ ,  $OY$ , and  $OZ$  are taken parallel to those of the whole system under investigation, the general coordinates of  $P$  with respect to the coordinate-axes of the system will appear also in the analytical expressions which determine the image  $f$  with respect to the axes  $X$ ,  $Y$  and  $Z$ .

A velocity, a force, etc., may thus be represented by a heteropolar vector (arrow) in  $P$ , determined by direction and magnitude, and having the symmetry  $C_{\infty}^F$ . But there are a number of physical phenomena for which the choice of the "image" in every point  $P$  of the system is not so simple: in the case of a liquid endowed with optical activity e.g., the symmetry may be represented by a portion of a small screw, with its axis varying in direction from one point to the other.

In this connection it may be remarked that a body or a medium in which all kinds of physical phenomena can take place, may be considered with respect to its symmetry-properties from several standpoints: we can speak of the symmetry of the medium itself, in as far as that symmetry is attributed to it regarding its molecular arrangement (crystals e.g.), or with respect to the whole complex of phenomena observed in it; or we can more particularly draw attention to the symmetry of the medium with respect to a certain group of phenomena, or finally with respect to a special phenomenon only. In a similar way we can speak of the symmetry of a group of phenomena, or of the symmetry of a special phenomenon. In all such cases we must know either the effects produced, or the causes which produce these effects; and the above mentioned image  $f$  must represent certain elements of symmetry which we attribute to the effects, or to the causes, if it should be considered really to fulfil the condition that it gives a *complete* description of the peculiarities of the phenomenon under investigation. If this be the case, the image  $f$  is indeed suited to its purpose; and then it will be possible for us to bring the considerations on symmetry-properties, as developed in the previous chapters, into the range of the phenomena investigated.

**§ 10.** With respect to the connection of the symmetry of causes and of the effects produced by them, we can now conclude from the facts observed up till now, that differences of symmetry in the causes, or in the special circumstances, *can* generally be manifested also in the effects produced, but that this is *not absolutely necessary* in every case. On the other hand: differences of symmetry in the effects observed can *only* be possible, *if they are present likewise in the determining causes or circumstances*.

A pencil of polarised light travelling in the ether, has undoubtedly a lower symmetry ( $D_2^H$ ) than the ether itself ( $K_{\infty}^H$ ), which lower symmetry is of course connected with the absence of certain symme-

try-elements in the luminous source from which the polarised light takes its origin.

But the *whole* complex of light-phenomena (radiations) in the ether, or in a crystal of *calcite*, etc., caused by this luminous source, has certainly the *same* symmetry ( $K_{\infty}^H$ ) as that of the ether, or a *higher* symmetry ( $D_{\infty}^H$ ) than that of the *calcite*-crystal.<sup>1)</sup>

From this and analogous examples we can in general conclude that a lack of symmetry-properties in the causes of physical phenomena, *can*, (and in by far the greater number of cases *will* really) be manifested also as a lack of symmetry-properties of the effects produced, but that this need not be always the case. From the absence of symmetry-properties in the effects observed however, it is certainly *necessary* to conclude, that there is a similar lack of symmetry-properties in the producing agents.

In other words: *the effects may have occasionally the same or a higher symmetry than the producing causes, but the last cannot have a higher symmetry than the effects observed.*

It is moreover worth remarking in this connection that symmetry-properties which are present in *all* causes, and in *all* circumstances governing a certain phenomenon, are necessarily always found in the effects produced also. However we must always be sure that the number of causes considered is really complete; evidently it is in many cases hardly possible to get full assurance of this.

§ 11. After the general remarks on the dependence of the symmetry-character of causes and effects in physical phenomena, we return to the consideration of some special symmetry-properties of certain physical states and to the question, in what way several simultaneously acting causes can cooperate as a resulting cause, producing certain effects.<sup>2)</sup>

If a crystal of *calcite* is traversed by rectilinear polarised light, and if we wish to give an exhaustive description of the way in which the propagation of light-waves takes place therein, experience teaches us that it is sufficient for this purpose, if we adopt as the "image" of the phenomenon in every point *P* a rotation-ellipsoid

<sup>1)</sup> The "image" *f* of the phenomenon of the propagation of rectilinear polarised light in a *calcite*-crystal, can be represented by a rotation-ellipsoid in every point *P*, with its axis of isotropy parallel to the trigonal axis of this ditrigonal crystal. (See below).

<sup>2)</sup> Cf. P. Curie, Journal de Physique. (3). 3. 407. (1894); Bull. de la Soc. Min. 7. 89, 418. (1884).

of certain dimensions and with its axis of isotropy parallel to the ternary axis of the crystalline medium. The symmetry of the image  $f$  is now, as already stated,  $D_{\infty}^H$ , while that of the crystalline medium, as concluded from its molecular structure, or from its cohesion-phenomena, is only that of the group  $D_3^D$ . The last group is a subgroup of  $D_{\infty}^H$ , — a fact to be remembered in what follows.

In the same way, if we ask: what symmetry is to be attributed to the *homogeneous electric field*, — as e. g. it may be produced between two parallel, infinitely extended, condenser-plates, — the answer is that we can attribute to it the symmetry of the group  $C_{\infty}^V$ , the parallel lines of force of the field having the direction of the axis of isotropy  $A_{\infty}$ .

If now the last mentioned symmetry is given to the image  $f$  which describes the physical state in every point  $P$  of the electric field, the question may rise, whether the special symmetry of the image  $f$  describing the physical state in every point  $P$  of the *homogeneous magnetic field* be the same, or perhaps another?

Now it is a well-known fact that the action of a magnetic field in each point  $P$  can be imagined to be produced by an electric current of a definite direction, flowing in a circular circuit round  $P$  as its centre, and with its plane perpendicular to the lines of force of the magnetic field. The image  $f$  in  $P$  therefore may be suitably taken as a circle with  $P$  as centre, with its plane perpendicular to the parallel lines of force of the field, and with a heteropolar vector (arrow) indicating in every point of the circuit the intensity and direction of the current.

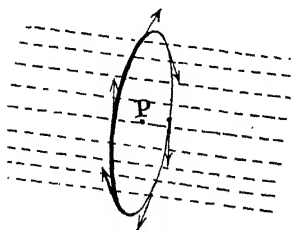


Fig. 93.

From this it follows that the homogeneous magnetic field can have *neither* planes of symmetry passing through its axis of isotropy, *nor* binary axes perpendicular to the lines of force. Moreover, if the field is reflected in a mirror

perpendicular to the lines of force, the direction of the current in the mirror-image so obtained is evidently the same as in the original field. The action of the field remains therefore unchanged by the reflection.

In other words: *the magnetic field must itself possess a plane of symmetry perpendicular to its lines of force, and a centre of symmetry also.*

Thus we are compelled to attribute to the homogeneous magnetic field the symmetry of the group  $C_{\infty}^H$  previously mentioned.

It is worth while remarking here, that this result is essentially dependent on the symmetry attributed above to the electric field, or to the electric current ( $C_{\infty}^V$ ). Indeed, the connection between the different physical phenomena, as proved by experience, makes it necessary that definite relations must also exist between their special symmetries. If for some reason or other we had primarily attributed the symmetry  $C_{\infty}^H$  to the electrostatic field, we should have to give to the magnetic field the symmetry previously attributed to the electric field, i.e.  $C_{\infty}^V$ . The electro-magnetic phenomena themselves determine this reciprocal relation: and the whole question is, as closer examination shows, evidently settled, as soon as it has become clear *what* one wishes properly to consider as the "mirror-image of an electro-magnetic field" <sup>1)</sup>.

If it be postulated that also in "the mirror-image of the electro-magnetic field", the general relations between electric and magnetic quantities shall *preserve* their validity, and that therefore the said mirror-image also shall have the function of a *possible* electro-magnetic system, then we have to decide which of the two following standpoints we wish to adopt:

a. Either in the mirror-image we can take as electric vectors (electric force, current, dielectric polarisation) the mirror-images of the original electric vectors, and as magnetic vectors (magnetic force, magnetic induction, etc.) the *inversed* mirror-images of the original magnetic vectors;

b. Or in the mirror-image we can take as magnetic vectors the mirror-images of the original magnetic vectors, and as electric vectors the *inversed* mirror-images of the electric vectors in the original electro-magnetic field.

In fixing our choice in the way first mentioned, we have in a homogeneous electric field symmetry-planes passing through the lines of force, in the magnetic field however a single symmetry-plane perpendicular to the lines of force. But in fixing our choice in the second way, the functions of the electric and magnetic fields are exactly interchanged.

Now there are "mechanical" theories of the electro-magnetic field, which are founded on the first conception; but there are also

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<sup>1)</sup> On this side of the problem my attention was kindly drawn by prof. H. A. Lorentz, to whom I am indebted for some valuable remarks here.



theories, which start from the second point of view. However, if we should wish to describe the electro-magnetic phenomena in certain cases by the *motion of ions or electrons*, — which has many and well-known advantages, — the *first* standpoint is certainly more convenient. These motions then, and the moving ions or electrons themselves can be looked upon as reflected in a plane, and it might be imagined that electric charges are attributed to the "reflected ions" or electrons with the same algebraic sign as they have in the original electro-magnetic field. In this way a description of the phenomena in the "mirror-image" will be possible just in the same way as if we were dealing with the original field; and the mirror-image is thus in truth a "possible" electro-magnetic system, fulfilling the above mentioned condition of the preservation of the general relations between the electric and magnetic parameters.

From this it will now be clear that the symmetries attributed to physical phenomena are really *relative* symmetries, determined by the general relations between the different natural phenomena themselves, and by the particular choice of the symmetry primarily given to a certain phenomenon which is considered as the starting-point for the definition of the others related to it.

§ 12. The symmetry of the "image"  $f$  in any point  $P$  of a physical system determines the *maximum* symmetry compatible with the occurrence of the phenomenon considered in  $P$ . The phenomenon, namely, can occur in a medium, if its symmetry be the *same*, or if it be that of a *sub-group* of the symmetry characteristic for the phenomenon in question.

If we have a crystal of *turmaline* whose symmetry with respect to the cohesion-phenomena (which are closely related to its internal structure), is that of the group  $C_3^I$ , and if this crystal be heated uniformly to a certain temperature, the symmetry of the crystal is of course by this scalar change altered in no respect; it remains, as before,  $C_3^I$ . But  $C_3^I$  is a sub-group of  $C_\infty^I$ ; and therefore the *possibility* exists that a *dielectric polarisation*, the symmetry of which is precisely  $C_\infty^I$ , will occur in the heated crystal. Nevertheless nothing has yet been said about the true *magnitude* of the expected phenomenon, nor about the real *necessity* of its occurrence. It is possible that the effect is for instance so extremely small, that it cannot be tested by any experimental method now available <sup>1)</sup>.

<sup>1)</sup> It is a curious fact, for instance, that the theory of Stokes on the conductivity of heat in certain crystals, as *scheelite*, etc., could not be verified

The same is the case if a crystal of *quartz* be compressed homogeneously parallel to the direction of one of its heteropolar binary axes: the direction of the binary axis remains heteropolar as before, so that an electric potential-difference can eventually occur at both its ends. Similar symmetry-relations occur if a planparallel crystal-plate, cut perpendicular to a binary axis, be compressed in the direction of the ternary axis of the quartz-crystal. In the two cases here considered, this dielectric polarisation could really be detected by experiment, because its magnitude was sufficient to be measured.

That such phenomena now really can occur in a crystalline medium which has the symmetry of a sub-group of that group, to which the proper symmetry of the phenomenon under investigation belongs, is elucidated by the fact that the symmetry of a crystalline medium is in reality a *minimum* symmetry, namely the *lowest* degree of symmetry, beneath which the symmetry of any physical phenomenon whatever observed in the crystal, can *never* sink. For many phenomena occurring in the crystal the special symmetry in truth appears to be much higher than that attributed to the medium itself according to its cohesion and molecular structure, i. e. than that of the "crystal-class", to which it belongs. These higher symmetries of the phenomena observed are such that certain symmetry-elements which are characteristic of these phenomena under *all* circumstances, are added to those of the crystal-class to which the crystal belongs.

§ 13. As an illustration of this we wish to consider the symmetry which a crystal will manifest with respect to the diffraction of Röntgen-rays, if a planparallel plate cut from it in some known direction be traversed by a narrow pencil of such rays perpendicular to its surface. This highly important phenomenon was discovered by Von Laue<sup>1)</sup> some years ago, and has since been studied by several investigators in different ways, and with particular success by Bragg Sr. and Jr.<sup>2)</sup>. However we will not consider these

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by experiment until now. The existence of the so-called "rotatory coefficients" in the equations of Stokes' theory, could never be demonstrated up to this date; cf. C. Soret, Journ. de Physique (2) 2. 241. (1893); Archives d. Sc. phys. et nat. de Genève, (3). 29. 355. (1893); *ibid.* 32. 631. (1894).

1) M. Von Laue, Friedrich and Knipping, Sitz. Bayr. Akad. d. Wiss. München, (1912), p. 303.

2) W. H. and W. L. Bragg, Proceed. Roy. Soc. London, 89. A. 277, 477. (1913); Zeits. f. anorg. Chemie 90. 255. (1914).

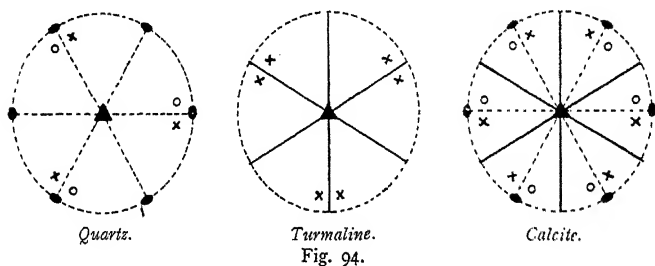
For the special questions dealt with here, see the papers of: G. Friedel, Compt. rend. de l'acad. d. Sc. Paris, 157. 1533. (1913); F. M. Jaeger and

remarkable and fundamental investigations in detail now, but only draw attention to the question of the symmetry of the obtained Röntgen-patterns.

Now the close analogy of the Röntgen-radiation with that of common light, is also expressed in the fact that under *all* circumstances the Röntgen-radiation is a *centrally-symmetrical* phenomenon too, every Röntgen-ray having a centre of inversion.

The result obtained in crystals must therefore, according to what was said before, always be as if the inversion were added to the characteristic symmetry-properties of the crystal; i. e. if the patterns obtained originated from a crystal whose symmetry in comparison with the actual one is enriched by a centre of symmetry.

Let us see if experience is in accordance with this conclusion. For that purpose we will compare the results obtained with plates similarly cut from the trigonal crystals of *tourmaline*, *calcite*, and *quartz*, which have successively the symmetry of the groups  $C_3^V$ ,  $D_3^D$ , and  $D_3$ , being thus radically different in this respect in all three cases.



In *fig. 94* the projection-figures drawn after Gadolin's method, may elucidate the arrangement of the different symmetry-elements in the three minerals considered.

We will suppose that sections through these crystals are prepared parallel to the basal plane (0001), to the prism-face (10 $\bar{1}$ 0), and to the face ( $\bar{1}$ 2 $\bar{1}$ 0) of the second prism.

In *tourmaline* the basal section has thus a ternary axis and three symmetry-planes perpendicular to it, the section (10 $\bar{1}$ 0) has no symmetry-element whatever perpendicular to it, while the section

( $\bar{1}2\bar{1}0$ ) has only a vertical plane of symmetry, perpendicular to the surface of the crystal-plate.

In *quartz* the basal section has only a ternary axis perpendicular to it, the section ( $10\bar{1}0$ ) has no symmetry-elements whatever perpendicular to its plane, and the section ( $\bar{1}2\bar{1}0$ ) has only a binary-axis perpendicular to it.

In *calcite* the basal section has a ternary axis and three planes of symmetry, all perpendicular to it; the section ( $10\bar{1}0$ ) possesses a vertical plane of symmetry perpendicular to its surface, and the section ( $\bar{1}2\bar{1}0$ ) has a binary axis perpendicular to its plane.

The Röntgen-radiation however has in all circumstances a centre of inversion. Thus, if this symmetry-centre, according to the thesis above explained, be added to the symmetry-elements of the three crystals considered, the symmetry of the *calcite* will *not* appear to alter, because *calcite* has itself such a centre of symmetry already. But if we remember (p. 15) that the combination of a binary axis and a symmetry-centre has as a consequence always the existence of a symmetry-plane perpendicular to that axis, and vice versa, — it will be evident that in *quartz* there will be produced three planes of symmetry by the addition of the symmetry-centre mentioned, which planes are all perpendicular to the binary axes already present, and thus will bisect the angle between both the others, at the same time passing through the ternary axis of the crystal.

In the same way in the *tourmaline*-crystal three binary axes perpendicular to the existing vertical symmetry-planes will be produced by the addition of the symmetry-centre, and of course these axes will bisect the angle between every pair of successive planes of symmetry. The symmetry of both kinds of crystals thus will evidently be changed into the same as that of *calcite* ( $D_3^D$ ). The result is therefore that the Röntgen-patterns obtained in all three cases will show the same symmetry, as if they originated from three crystals, every one of which possesses the symmetry of the group  $D_3^D$ .

If the sections parallel to ( $0001$ ), ( $10\bar{1}0$ ), and ( $\bar{1}2\bar{1}0$ ) are traversed by a thin pencil of Röntgen-rays exactly perpendicular to their surfaces, the result will be that the patterns obtained

with a crystal-plate parallel to ( $0001$ ) will show a ternary axis and three symmetry-planes perpendicular to the plane of the photographic plate;

with a crystal-plate parallel to ( $10\bar{1}0$ ) will show a single vertical plane of symmetry perpendicular to the photographic plate;

with a crystal-plate parallel to  $(\bar{1}2\bar{1}0)$  will show a single binary axis perpendicular to the photographic plate.<sup>1)</sup>

In fact, our experiments completely confirm the conclusions drawn here. In *fig. 95 a-c*, *96 a-c*, and *97 a-c* the stereographical pro-

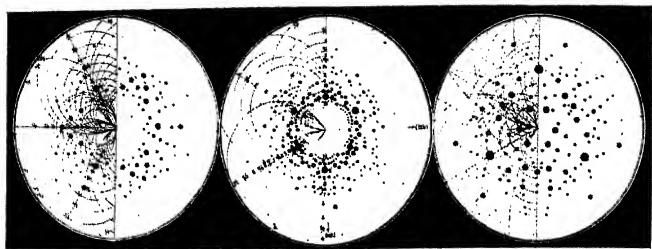


Fig. 95 *a-c*.

Stereographical Projection of the Röntgen-patterns of *quartz*, *tourmaline* and *calcite*. Plates parallel to  $(0001)$ .

jections of the Röntgen-patterns are reproduced, as they were obtained by H. Haga and the author<sup>2)</sup> in the case of the three

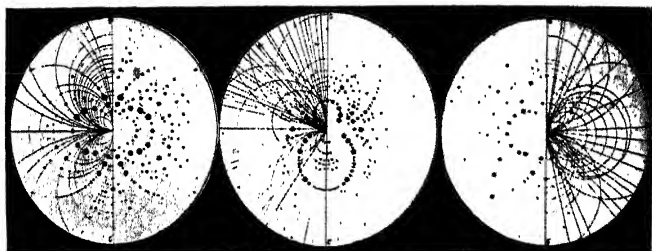


Fig. 96 *a-c*.

Stereographical Projection of the Röntgen-patterns of *quartz*, *tourmaline*, and *calcite*. Plates parallel to  $(10\bar{1}0)$ .

minerals discussed here. There can be no doubt whatever about

<sup>1)</sup> A binary axis perpendicular to the photographic plate, manifests itself in the photographs as a centre of symmetry in it; a centre of symmetry in the crystal is *not* manifested in the pattern itself.

<sup>2)</sup> H. Haga and F. M. Jaeger, *Proceed. Akad. v. Wetenschappen Amsterdam*, Vol. 17, 18, (1914-'16). On accidental abnormalities of the patterns of *quartz* caused by twinning, *vid. the papers mentioned here*.

the full agreement between the experimental result and the theoretical deductions.

That in *all* cases of crystalline symmetry this agreement really takes place, and that therefore reversely it may be safely concluded, that the Röntgen-radiation is in *all* circumstances actually a *centrically-symmetrical phenomenon*, was demonstrated for the first time by the same authors<sup>1)</sup> in a series of papers, in which were described experiments with crystals of almost all the 32 classes of crystallography.

If accidental abnormalities caused by occasional irregularities of the molecular structure, or by twinning-phenomena, be leaved out of account here, we can say that the *centrically-symmetrical nature of the radiation considered*, as well as the agreement of theoretically

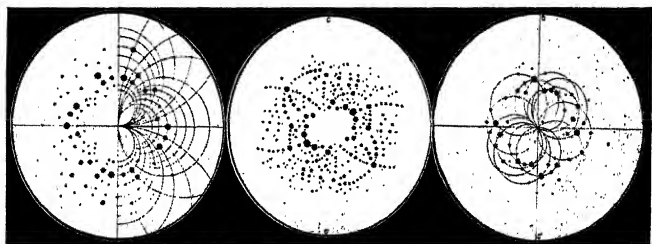


Fig. 97 a - c.

Stereographical Projection of the Röntgen-patterns of *quartz*, *tourmaline*, and *calcite*. Plates parallel to  $(1\bar{1}210)$ .

*expected and experimentally found symmetry of the Röntgen-patterns, has now been exactly stated in all cases.*

§ 14. The same thesis about the increase of symmetry of a crystalline medium, in which a phenomenon of a special symmetry occurs, appears to be true for all other physical phenomena in crystals. In the same way we find that the 32 possible symmetry-classes of crystallography are reduced to the following eleven:

$I$ ,  $C_2^H$ ,  $D_2^H$ ,  $C_4^H$ ,  $D_4^H$ ,  $C_3^I$ ,  $C_3^D$ ,  $C_6^H$ ,  $D_6^H$ ,  $T^H$ , and  $K^H$ .

for all phenomena which have likewise a *centrically-symmetrical* character.

We may also ask: to which and to how many classes will the phenomena of *pyro-* and *piezo-electricity* appear to be restricted, — phenomena for which the *absence of a symmetry-centre* appears to be precisely the striking feature?

According to a theory of W. Voigt <sup>1)</sup> on pyro- and piezo-electric phenomena in crystals, in which the electric momentum in such crystals is thought to be determined by the *deformations* which are the consequences of the temperature-changes, and of the compressions or dilatations to which the crystal is subjected, the said phenomena may occur in *twenty* of the 32 crystal-classes: of course they will *not* be manifested in the eleven centrically-symmetrical crystal-types just mentioned above, or in the crystals of the group *K*, which do not possess any heteropolar axes. In the remaining groups such dielectric polarisation may occasionally occur, if circumstances are advantageous; and the difference of potential can then manifest itself at both ends of any heteropolar axis.

In an analogous way we can answer the question: to how many symmetry-classes will the number *thirty-two* be reduced, if the physical phenomena considered should be described by means of an "image" *f*, having the shape of an ellipsoid? Such is the case in the phenomena concerning the propagation of light-waves, of heat, of electric currents, of magnetic induction, etc. <sup>2)</sup>. The number of the possible symmetry-groups will then appear to be reduced yet more, as is universally known to every mineralogist with respect to the optical properties of crystals.

§ 15. Something analogous to what was said in the case of physical phenomena occurring in crystalline media of a certain symmetry, will be the case if two physical causes, each having its own symmetry-character, be superposed in such a way that each of them can contribute its share to the resulting effect. The resulting cause then will act as having only the symmetry-elements *which are common to both component causes*. The symmetry of the resulting effect will thus be commonly also of a *lower* degree than that of each of the causes separately; but as we have already mentioned, this *need not* always be the case, the effect having possibly also a *higher* symmetry. If *all* determining causes of the effects finally produced were fully known, *then* of course the symmetry-elements appearing the complete set of causes must be characteristic also of the special symmetry which is exhibited by the effects produced <sup>3)</sup>.

<sup>1)</sup> W. Voigt, Abh. der Ges. der Wiss. Göttingen, **36**. (1890).

<sup>2)</sup> Th Liebisch, Grundriss der physikalischen Krystallographic, (1896), p. 177—183.

<sup>3)</sup> The theorem that a certain lack of symmetry-elements in the causes will usually manifest itself by the lack of certain symmetry-elements of the effects,

The group  $C_\infty$  is a common sub-group of the symmetry-groups  $C_\infty^V$ ,  $C_\infty^H$ , and  $D_\infty$ . If now two causes having the symmetry of two of the groups last mentioned, be superposed in the way stated, they will act as a single cause having the symmetry  $C_\infty$ , and the effect produced will have this symmetry or that of the higher symmetrical group  $C_\infty^V$ . Some examples will make this clear.

If a soft iron rod, past which is sent an electric current ( $C_\infty^V$ ), be placed simultaneously in a homogeneous magnetic field ( $C_\infty^H$ ), the lines of force of which are parallel to the direction of the rod and of the current, the iron rod will show a *torsion* ( $D_\infty$  or  $C_\infty$ ), produced by the cooperation of both causes. Indeed, with the apparatus shown in *fig. 98*, this effect (Matteucci-Wiedemann)<sup>1)</sup> can be easily demonstrated, even as a lecture-experiment. The thick iron-wire  $l$ , bearing at its one end a weight  $P$  of about 100 grams, can turn freely round a sharp steel-axis  $e$ , placed in the mercury-cup  $Q$ . The current is introduced through the mercury and the steel-axis  $e$ . The sudden magnetisation of the iron-wire is brought about by means of a solenoid  $S$ , and the resulting torsion is demonstrated by the deviation of a light-beam reflected at the small mirror  $a$ , which is fixed to the steel-axis.

This deviation can be made visible to an audience by means of a divided scale on the wall of the lecture-room.

The dependence of the direction of the torsion on that of the current and the magnetic field ( $N$  = north,  $S$  = south pole), is shown in *fig. 99*; this drawing needs no further comment.

Evidently we have to deal with the superposition of two causes having the symmetries  $C_\infty^V$  and  $C_\infty^H$ , with their axes of isotropy

needs some further comment. It holds only, if the causes be independent of each other, if no one of them be preponderant in its influence, and if the number of the governing causes be a limited and a relatively small one. If this number however is *very great*, as e.g. in cases where merely *statistic* effects are considered, the dissymmetry of one or more causes is, or at least need not be manifested as a dissymmetry of the effects produced by their cooperation (J. C. Kapteyn, *Skew frequency-curves in Biology and Statistics*, Groningen, 1916). In physical phenomena however, the number of producing causes is never a very great one; in such cases the considerations held here, will certainly be of use.

<sup>1)</sup> C. Matteucci, *Ann. de Chim. et Phys.* (3). **53**. 385 (1858); G. Wiedemann, *Pogg. Ann.* **103**. 571. (1858); **106**. 161 (1859); *Baseler Verh.* **2**. 169 (1860); E. Villari, *Pogg. Ann.* **137**. 569. (1869); G. Gore, *Proceed. Roy. Soc. London.* **22**. 57 (1874); *Transact. idem*, (1874). 529.



parallel to each other, giving as effect a torsion of the symmetry  $D_\infty$  or  $C_\infty$  as a result. In accordance with the fact that these relations between the three groups are *reciprocal*, — a magnetised steel-wire if twisted by a force at both its ends, will show a difference of potential (current) produced in it, the presence of which

can be easily demonstrated by the induction-current it produces in an encircling solenoid. Here also the superposition of the magnetic field ( $C_\infty^H$ ) and the torsion ( $D_\infty$ ) or  $C_\infty$ , will have a result of the symmetry  $C_\infty$ , and this group  $C_\infty$  being a sub-group of  $C_\infty^H$ , the occurrence of an electric current having the latter symmetry, is compatible with the superposition of both causes.

In the same way a soft iron rod will become a magnet if an electric current passes through it, while being twisted by a force applied to one of its ends; the other end is held fast. This phenomenon also can easily be demonstrated by means of the induction-current the magnet will produce in an encircling solenoid. It is a fact worthy of attention that the free electrons of the iron rod, moved by the electric force, are *not* the same as the electrons which are attached to the iron-atoms themselves, and whose motion is the cause of Ampère's "molecular currents".

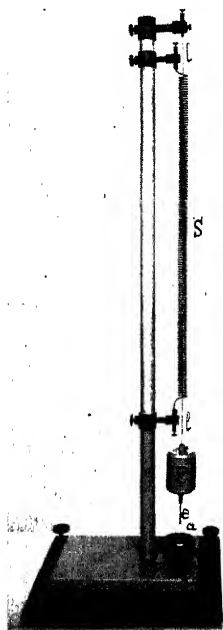


Fig. 98.

The kinetic energy of both kinds of electrons in the metal must therefore be interchanged to and fro in some way or other, because in experiments like these, there must evidently exist definite connections between them.

§ 16. French authors especially<sup>1)</sup> have frequently pointed to the fact that for the description of physical relations, it often is more desirable to bring to the fore *the absence of some symmetry*—

<sup>1)</sup> Vid. i. a.: L. Pasteur, Deux Leçons sur la Dissymétrie Moléculaire, professées devant la Société Chimique de Paris (1860); P. Curie, Journal de Physique, (3). 3. 407. (1894).

*properties* (i. e. *dissymmetry*), rather than to deal with the presence of other symmetry-properties, as we have done in the preceding paragraphs. Indeed, in the course of our considerations we have already been able to draw attention to this fact.

If in a crystalline medium there is *no* centre of symmetry, or if the principal axis of a crystal be heteropolar, i. e. if *no* binary-axes, *nor* a symmetry-plane be perpendicular to it, — then the *absence*

of these symmetry-elements will make it possible that an electric field with a symmetry  $C_{\infty}^V$  eventually occurs, in which the symmetry-centre, the binary-axes, and the symmetry-plane perpendicular to the lines of force, are also lacking. The same is the case if two causes are superposed to a resulting cause which gives an effect in which both components take a part. If the superposition of an electric and

a magnetic field occurs in such a way that their axes of isotropy are not parallel, but perpendicular to each other, the only remaining symmetry-element of the resulting cause is a plane passing through the axis of the electric field, and perpendicular to the magnetic lines of force.

The electric current, which in this arrangement of both fields is observed in crystallised *bismuthum* (Hall-effect), may be considered as an effect, the occurrence of which is in full accordance with the *absence* of definite symmetry-elements in the producing cause. For such electric current has *no* plane of symmetry perpendicular to its direction; therefore at least in one of its causes must lack that symmetry-element too. Now in the above mentioned superposition, conditions have become such as to make the occurrence of the electric current possible: neither the electric field alone, nor the magnetic field alone, can be the cause of the Hall-phenomenon in a direction perpendicular to the plane of the current and the magnetic lines of force; but *if both be combined*, the symmetry-centre of the magnetic field, as well as the symmetry-planes of the electric

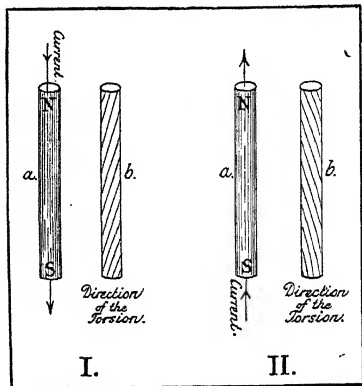


Fig. 99.

field, — with the exception of the single one just mentioned, — will *disappear*, and *now* really all circumstances of symmetry (or of dissymmetry) in the resulting cause will become such as to be compatible with an eventual occurrence of the electric current ( $C_{\infty}^V$ ) as is observed in the Hall-effect.

In the same way the motion of the string in Einthoven's string-galvanometer, or that of the electric arc in the Birkeland-Eyde-furnaces, will be symmetrical with respect to a plane passing through the electrodes, or perpendicular to the lines of force of the magnetic field applied.

However the *magnitude* of such a predicted or expected effect must be investigated in every case by special experiments; as already stated, it may be too insignificant as to be detected by the usual experimental methods. The general reasonings only teach us that, *if* such an effect be produced by two superposed causes, the *dissymmetries* of the last are *added to each other*, and the symmetry of the effect must be in accordance with the *higher* degree of *dissymmetry* (i. e. the *lower* symmetry) thus produced.

The views concerning the symmetry or the dissymmetry of causes and effects, are principally identical: but, in the one case is the chief attention drawn to the symmetry-properties *still present*, in the other case to the symmetry-properties which have *disappeared*.

§ 17. Finally it may be remarked that a number of problems which can be answered only in the experimental way, are connected with the views developed in the preceding paragraphs.

If only the superposed physical conditions be such that an effect, resulting from the interference of them may be expected with some probability, it is worth trying such an experiment tentatively.

Thus it may possibly be found that a difference of potential would be observed with two electrodes plunged into a liquid of strong optical rotatory power, if this fills a tube and be placed in a strong homogeneous magnetic field, having its lines of force parallel to the axis of the tube and to the direction of an incident beam of polarised light; and vice versa.

If in a superposed magnetic and electrostatic field, with their lines of force parallel to each other, a chemical reaction takes place, in which a racemic acid or base combines with an inactive base or acid, it might under favorable circumstances perhaps be observed that the reaction-velocities of the dextro-, and laevogyrotory components of the racemic substance which combines with the inactive

compound, were *not the same*, and that an optical activity of the reaction-mixture were thus produced during the reaction. If such an effect could really be demonstrated, the fact would be of the highest importance with respect to the eventual *origin of the first optically active substances on earth*, i. e. with respect to the primitive question of the "asymmetrical synthesis" of organic molecules. It cannot be predicted *à priori* whether such effects will manifest themselves or not; and even if their possibility appear from theoretical reasons to be most probable, their magnitude, as was already stated, may be so small as not to be detected by any experiment. Only continual attempts in this direction can bring real progress in such cases. Perhaps promising experiments of this kind could be made by investigating the influence of superposed magnetic and electric fields on crystallisation-phenomena of salts containing *iron, cobalt* or *nickel*; or by trying to establish the fact of the predominant crystallisation of one enantiomorphous crystal-form from solutions of substances such as *sodium-chlorate*, the molecules of which are doubtless themselves enantiomorphous, and can evidently congregate to dextrogyrate or laevogyrate structures.

It would be of interest also to investigate, if a substance the molecules of which have an enantiomorphous or asymmetrical structure, would possibly show a magnetic polarisation, if placed in a strong electrostatic field. Objects of this kind might be found amongst the crystals of the remarkable mirror-stereoisomerides of complex salts, as  $\{Co(Eine)_3\}X_3$ , and  $\{Fe(Phen)_3\}X_2$ ; etc.<sup>1)</sup> Some experiments with these objects and others, on the relative decomposition-velocities of both antipodes in photochemical reactions under the influence of dextro- or laevogyrate, circularly polarised light, have been started in the author's laboratory.

§ 18. Finally some very short remarks on another subject. In the preceding paragraphs we have *not* dealt with the symmetry in the arrangement of *numerical* data as they are often found as the result of *statistic investigations* on a great number of facts, because this subject is, properly speaking, merely a chapter of pure mathematics.

That there are often to be detected *symmetrical arrangements* of such numbers in cases of numerical arrangement, where series of

<sup>1)</sup> In these formulae: *Eine* = *Ethylene-diamine*:  $C_2H_4(NH_2)_2$ , and *Phen* = *α-Phenanthroline*:

such data are considered, to which the calculus of probabilities (frequency-curves, etc.<sup>1)</sup> can be applied, is a well-known fact (binomial coefficients, etc.) This symmetry manifests itself for instance in the numbers obtained by Gr. Mendel in his famous researches concerning the heredity of properties in plant-hybrids, and in the corresponding work of several other investigators.<sup>2)</sup>

Instances of this kind may easily be augmented; however it is not our purpose to go into particulars here, but simply to draw the attention of the reader also to these occurrences, which represent more especially a chapter of the general theory of numbers.

About the symmetrical arrangement of some organs in plants, — a problem which is closely related to the kind of problems mentioned here, — we will say something at the end of the next chapter.

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1) J. C. Kapteyn, Skewfrequency-curves in Biology and Statistics, Groningen, (1916).

2) Gr. Mendel, Versuche ü. Pflanzenhybriden, Verh. naturf. Verein. Brünn, 4. 3—47 (1865); Ostw. Klass. d. ex. Wiss. No. 121. (1901), p. 17; Cf. also: J. Tammes, Rec. des Trav. botan. Néerl. 8. 232. (1911).

## CHAPTER VI.

The Periodical Repetition of Identical Units in a Plane. — The Repeat as the Unit of an Endless Pattern. — Homogeneity in Periodical Arrangements. — Homologous Points. — The Homogeneous Distribution of Points in a Plane. — The Net-Plane. — The Netplane-structure in Endless plane Patterns. — The Symmetry of a Pattern and of its Net-plane. — Points regularly distributed in Space. — The Space-lattice. — Some general Properties of Space-lattices. — The Symmetry of Bravais' Space-lattices. — Elements of Pseudo-symmetry. — General Symmetry-Relations in Endless Systems. — The Problem of the General Deduction of All Homogeneous Arrangements in Space. — The Fundamental Domain in Endless Homogeneous Structures. — Enantiomorphism and Congruency of Structural Units. — The Theories of Sohncke, Von Fedorow, Schoenflies. — General Results. — Endless Periodical Patterns and Crystal-structure. — The Crystal as a Tridimensional Symmetrical Pattern. — Continuous and Discontinuous Properties of Crystalline Matter. — The Space-lattice as a Geometrical Expression of Haüy's Law. — The Chemical Structure of Crystals: various Ideas. — Barlow-Pope's Theory of the Unit-stere. — The Diffraction of Röntgen-rays in Crystals. — Some Remarks about the Investigations of Laue, Bragg, Debije. — The Deductions of Bragg concerning the Space-lattices of Crystals. — Some simple Examples. — The Chemical Molecule in the Crystalline State. — Molecular and Atomic Forces; Valency and Coordination. — The Periodical Arrangements in Living Nature. — Disposition of Leaves in Plants. Views on Phyllotaxis. — A Contrast between Inanimate and Living Nature with respect to the Manifestation of Symmetry. — Some Final Remarks.

§ 1. Hitherto we have dealt exclusively with the symmetry of *limited* systems. In such figures only a limited number of points correspond to each given point; the original point can successively be

made to coincide with some others by the non-equivalent operations of the symmetry-group to which the figure as a whole belongs.

But occasionally we have drawn attention to the fact that there are also figures in which an endless number of points may correspond to any given point; it may happen that no point of the system remains at its place in space, should the system be subjected to the set of non-equivalent operations characteristic of its symmetry. Such figures are called *endless, unlimited, or infinitely extended* figures.

It will be remembered that in Chapter II, several symmetrical operations were considered which have no real significance for limited figures, as, for instance, *translations, helicoidal motions*, rotations about axes or reflections in planes *not passing through the same point O in space*, etc. Such operations may however be of essential interest just for such *unlimited* systems.

A detailed account of the structure-theories and an exhaustive treatment of the remarkable properties of all possible unlimited symmetrical arrangements would be out of place here. We wish only to give an impression of the most salient features of such systems, and more particularly to show the importance of the views dealt with, for the problem of the internal structure of crystalline matter. As these views have in recent times met with most happy endorsement from direct experiments, it seemed desirable to dwell somewhat longer upon the results obtained in this way and upon the methods applied in these investigations. Finally, some remarks on arrangements of this kind as met with in living nature will be made with a view to drawing the attention of the reader to these applications of the doctrine of the regular unlimited systems, also in questions of the arrangement in space of the organs in living individuals. Even if only preliminary, and giving no true explanation of the mechanical and physiological causes governing the said phenomena, the views about them are suggestive enough to be worthy of more detailed examination in the future from the standpoint of the general doctrine considered in this book.

§ 2. If a plane figure be repeated again and again in the plane of drawing, in such a way that proceeding in some direction, we meet after equal distances identical and identically oriented figures, it may be said that the repetition of the original figures occurs *periodically*; the length of the distance between two consecutive figures in the same position is called the *period* of the arrangement in the direction considered. The complete, infinitely extended assemblage thus obtained

can be discriminated as a plane, endless *pattern*; the original figure, by the repetition of which the pattern is produced, may be called the *repeat* or the *motif* of it. The motif is the essential unit of the endless pattern, and the special nature of the latter is determined as well by the shape of this unit, as by the specific mode of its repetition. From what we have seen in the preceding chapters, we can conclude that "symmetrical" arrangements of a repeat have an essentially "periodical" character.

Moreover, if the arrangement be such that every repeat of it be surrounded by all others in the same way as every other motif is by the remaining, then we say that the pattern is *homogeneous*. The homogeneity of the pattern involves that its aspect will always be the same to an observer, if placed at any point whatever of the infinitely extended system.

In *fig. 100* a portion of a pattern is reproduced which shows clearly what is meant by this homogeneity; of course the pattern must be imagined to be infinitely continued in all directions of the plane. If  $A_1$  be a given point of the motif and  $A_2$  the corresponding point in the next figure, the line joining  $A_1$  and  $A_2$  will be parallel and equal to a number of other lines joining two corresponding points  $B_1$  and  $B_2$ ,  $C_1$  and  $C_2$ , in both pattern-units considered. The points  $A_1$  and  $A_2$ ,  $B_1$  and  $B_2$ ,  $C_1$  and  $C_2$  etc., are said to be *homologous points* of the pattern; round such homologous points the distribution of all other points in every pattern-unit is the same as in all other units of the pattern. The lines  $A_1A_2$ ,  $B_1B_2$ ,  $C_1C_2$ , are evidently equal and parallel to the *translation*  $FF'$  which brings the original motif  $F$  into the position of the next parallel figure  $F'$ . However it is easily seen that there are a number of other translations by which the original motif can be made to coincide with the surrounding figures  $F''$ ,  $F'''$ , etc., if it be shifted along various directions of the plane, such as  $A_1A_2$ ,  $B_1B_2$ ,  $C_1C_2$ , etc. If we do not consider the special shape of the repeat  $F$ , and simply take one of its points  $P$ , for instance its *geometrical centre*, we can describe the situations of all corresponding figures  $F'$ ,  $F''$ ,  $F'''$  by fixing only the final situations of the points  $P'$ ,  $P''$ ,  $P'''$ , which are the homologues of  $P$ , i.e. in the case considered: the *geometrical centres* of the figures  $F'$ ,  $F''$ ,  $F'''$ , etc. All these homologous points form together a plane system of homogeneously and regularly distributed points which, on closer examination, appear to be situated like the knots of a network with parallelogrammatic, rectangular, or quadratic meshes.



This plane system of points is therefore called a *net-plane* (fig. 101); and if in fig. 100 we had started with any other point of the motif

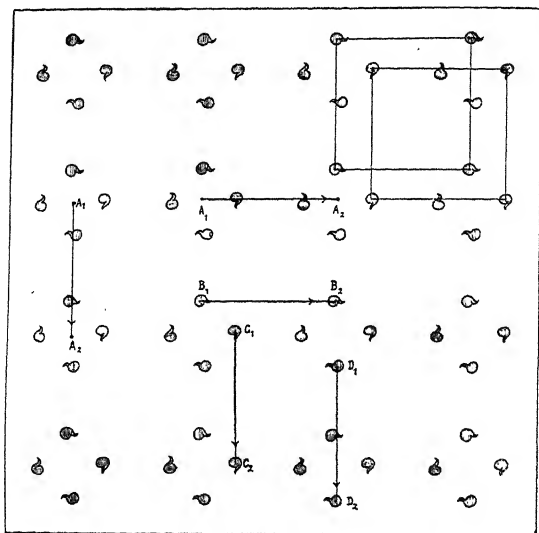


Fig. 100.

$F$ , for instance with  $Q$ , or  $S$ , or  $V$ , — we should in the same way have found a number of other endless point-systems  $QQ'Q''Q''' \dots$ ,

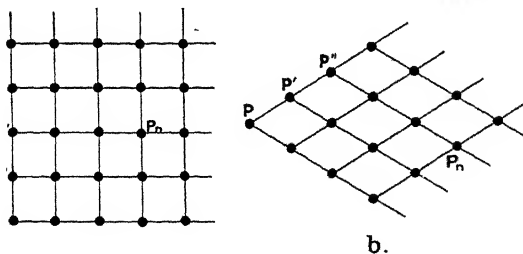


Fig. 101.

$SS'S''S''' \dots$ , etc. which are all *completely congruent* with the first system  $PP'P''P'''$ , and only with respect to the latter shifted along the directions  $PQ, PS, PV$ , etc.

From this it is clear that the proper character of the pattern is intimately connected with that of the net-plane  $PP'P''P'''$ , .... (or  $QQ'Q''Q'''$ , .... etc.), which is, in a sense, its very foundation.

§ 3. It is thus of high importance for the study of homogeneous distribution in general, to examine first the properties of such homogeneous and regular systems of mathematical points. If for the moment we make abstraction from the particular case of the distribution of points in a "plane" only, and if we extend our reasonings to *tridimensional* systems of points, asking what their

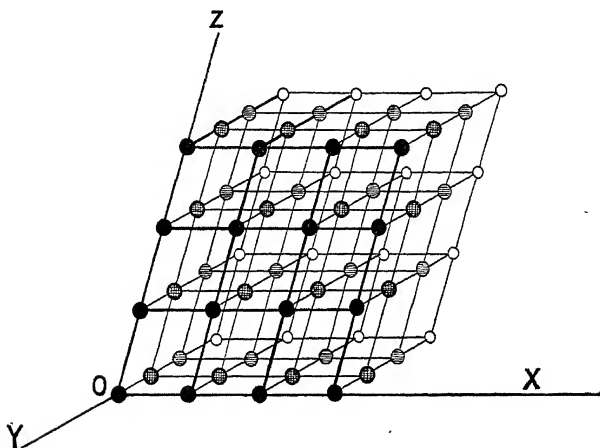


Fig. 102

arrangement in space must be in order to fulfil the condition of homogeneity as defined above, — the answer will evidently be, that these points must be situated at the corners of an infinite number of congruent and contiguous *parallelopiped cells*, in which space can be divided without leaving any room between them. In this way these points appear situated like the knots of a *net-work in space*, the meshes of which are the congruent and contiguously arranged parallelopiped cells just mentioned.

A general type of such network which bears the name of a *space-lattice*, is reproduced in *fig. 102*. Starting with a point  $O$ , we can look for the point  $P_1$  nearest to it at a distance  $d_1$ , then for the second nearest point  $P_2$  at a distance  $d_2$ , and finally for the third nearest  $P_3$  at a distance  $d_3$  from  $O$ . The directions of  $OP_1$ ,  $OP_2$ , and

$OP_3$  may be taken as axes of reference  $OX$ ,  $OY$ , and  $OZ$ ; then the parallelepipedon having  $d_1$ ,  $d_2$ , and  $d_3$  as its edges, is the absolutely determined, parallelepiped "unit-cell" of the infinitely extended space-lattice, and evidently *no other point of the latter is situated within this parallelepiped cell any longer*. The whole space-lattice might also be imagined to be built up by three sets of an infinite number of *net-planes*, all parallel to and equidistant from the three pairs of opposite limiting faces of the parallelepiped cell; and in the same way an infinite number of sets of parallel equidistant net-planes can be distinguished in the space-lattice, all made up by points placed at the corners of parallelogram-shaped meshes, while no other points are situated within the boundaries of these parallelograms.

The essence of a *space-lattice* is that it is a homogeneous and periodical structure of points, in which each point therefore is situated relatively to its neighbours in exactly the same way as every other point. The parallelepiped unit-cell represents the "geometrical period" of the space-lattice, and this period, although extremely small, is always a *finite* one. The orientation of every net-plane therein, is determined by the space-lattice alone; and to every net-plane there corresponds a set of an infinite number of congruent net-planes, all parallel to and equidistant from the first. Moreover the assemblage may possess special symmetry-properties by which the individual shape of the unit-cells and their marshalling are determined; in such a case the points will have a perfectly regular geometrical arrangement in which the various symmetry-elements will be associated according to the general rules of the doctrine of symmetry, as deduced in the preceding chapters.

§ 4. Before dealing with these symmetry-properties of space-lattices, it is of interest to consider some of their general properties in detail.

In the first place it is clear that the meshes of the various net-planes of a space-lattice are of different sizes, but constant for every net-plane of a certain situation. The parallelograms in the net-planes parallel to the coordination-planes, as determined above, evidently possess the three smallest areas which can occur at all in the space-lattice under consideration. Because the unit-cell of smallest volume has a constant volume, this surface of the meshes will be smaller in the same rate, as the distance between the equidistant net-planes of the same set is greater than in another

set.<sup>1)</sup> Thus if  $d_1 > d_2 > d_3$ , the meshes of the net-plane ( $d_2, d_3$ ) will have a smaller area than those of the net-plane ( $d_1, d_3$ ) or ( $d_1, d_2$ ), and more particularly will these areas be *inversely proportional to the distances  $d_1, d_2$ , and  $d_3$  respectively*. When we define the *density* of a net-plane as the number of meshes per unit of surface, this density  $\delta$  can be expressed by  $\frac{1}{\varepsilon}$ , in which  $\varepsilon$  is the surface of the parallelogram-shaped mesh of the net-plane. From what has been said, it is obvious that *the surface-density of net-planes is directly proportional to the distance between two of them in the same parallel set*. The further such parallel net-planes are distant from each other, the greater will their surface-density be, and reversely: *the distance between two parallel net-planes of a space-lattice is directly proportional to their surface-density*.

In the second place, if three axes of reference  $OX$ ,  $OY$ , and  $OZ$  be chosen, the distances of the successive points along them being  $d_1, d_2$ , and  $d_3$  respectively, then the coordinates of every point  $P$  of the space-lattice will be always  $pd_1, qd_2$ , and  $sd_3$ , in which  $p, q$ , and  $s$  are *integer numbers*. It may be easily conceived from this, how this fact involves that every net-plane passing through the point  $P$  intercepts on the three axes  $OX$ ,  $OY$ , and  $OZ$  segments, the length of which are always of the form:  $md_1, nd_2$ , and  $rd_3$  respectively,  $m, n$ , and  $r$  being such integer numbers too.

The significance of these considerations for the special problem of crystal-structure is evident, because the fact just mentioned is a direct geometrical expression of Haüy's law in-crystallography, concerning the rational indices of possible crystal-facets (see the previous Chapter).

§ 5. We will now examine the symmetry-properties of such space-lattices more closely, and in the first place draw attention to some general facts in connection with this symmetry.

Because every point of the endless space-lattice has wholly the same function as all other points, it must be at once clear that *every point of a space-lattice is a symmetry-centre of it*. A space-lattice

<sup>1)</sup> It can easily be demonstrated, that primary cells, i.e. such cells of the space-lattice which do *not* contain any other points within their parallelepiped volume besides those at the corners of it, have always *the same and minimum* volume.

A simple geometrical reasoning will convince us of this, and a similar thesis is valid for the primary meshes of a net-plane, i.e. for each mesh which contains no more points within its parallelogrammatical area.

is therefore always a *centrally-symmetrical* arrangement, and as the existence of this symmetry is equivalent to a symmetry-property of the *second* order, it follows from this that a space-lattice can *never* differ from its mirror-image. Its symmetry belongs in all cases to that of the symmetry-groups of the second order, and more especially to those amongst them which are characterised by the possession of a symmetry-centre. Of course this fact will at once restrict appreciably the number of eventually possible symmetrical arrangements of this kind.

A second universal property of space-lattices is that an eventual *symmetry-axis of it must always be parallel to, or coincident with a point-row of the space-lattice*; and moreover *each symmetry-axis must always be perpendicular to a net-plane of the space-lattice too.*

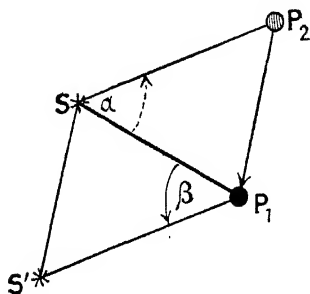


Fig. 103.

The truth of both these facts can easily be deduced from some simple geometrical reasonings.

Finally it will be clear that if a space-lattice has a symmetry-axis of the period  $\alpha = \frac{2\pi}{n}$ , not passing through a point of the system, it must have simultaneously *an infinite number of parallel* symmetry-axes of the

same period passing through every point of the space-lattice.

The truth of this can be demonstrated as follows. Let  $S$  (fig. 103) be the point of intersection of a symmetry-axis  $A(\alpha)$  with the plane of drawing; this plane, according to what is said above, is certainly a net-plane of the space-lattice, and therefore  $P_1$  may represent a point of it situated in it nearest to  $S$ .

If we turn the space-lattice round  $A(\alpha)$  through  $\alpha = \frac{2\pi}{n}$ , the point  $P_1$  comes into  $P_2$ , and  $P_2$  must therefore be also a point of the system. If this is now shifted along  $P_1P_2$ , until  $P_2$  coincides with  $P_1$ , the point of intersection  $S$  will have reached  $S'$ , while the point  $P_1$  will have returned to its original position.

Both successive operations are together evidently equivalent to a rotation about an axis passing through  $P_1$ , which brings  $S$  in  $S'$ , the period  $\beta$  of this axis also being  $= \frac{2\pi}{n}$ . It is demonstrated

therefore that there are really in all points  $P$  such axes parallel to the one supposed in  $S$ , and that all have the same period.

With respect to the possible combinations of symmetry-elements in such space-lattices, we can refer here to the contents of the preceding chapters *II* to *IV*; the general rules stated there are valid also here. The only question yet to be considered is: what can be the *periods* of the axes of symmetry in such space-lattices?

Let  $P$  (fig. 104) be a point of the system. Let us suppose that a symmetry-axis  $A(\alpha)$  of the period  $\frac{2\pi}{n}$  passes through  $P$ , and that it is perpendicular to the plane of the figure. According to the above, it is therefore at the same time a net-plane of the space-lattice. The point situated *nearest* to  $P$  in this net-plane may be  $N_1$ .

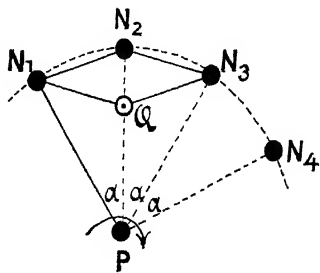


Fig. 104.

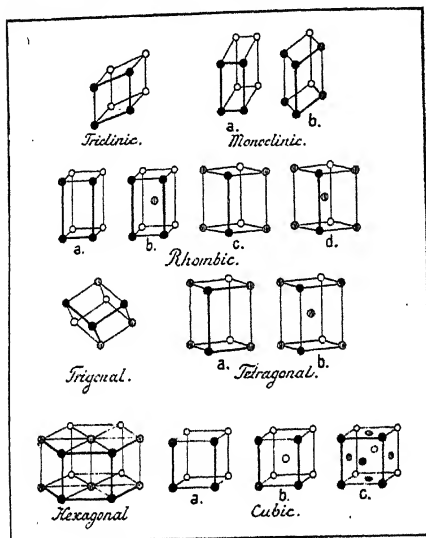
When we perform now the characteristic rotations round  $A$  through angles  $\alpha$ ,  $2\alpha$ ,  $3\alpha$ , etc., the point  $N_1$  reaches successively the corresponding points  $N_2$ ,  $N_3$ ,  $N_4$ , etc. of the net-plane. But because of the parallelogram-shaped meshes of this net-plane, a point  $Q$  must also be found in the net-plane in such a way that  $Q$ ,  $N_1$ ,  $N_2$ , and  $N_3$  together form a primary mesh of it. Moreover the coordinates of all these points in the net-plane must be in rational proportions to each other.

Now we have supposed that  $N_1$  was *nearest* to  $P$ ; the absolute distance  $PQ$  may therefore only be *greater*, or in the extremest case be *equal* to  $PN_1$ , etc. Now  $\frac{PQ}{PN}$  is evidently  $= 1 - 4 \sin^2\left(\frac{\pi}{n}\right)$ ; and if we calculate the values of this expression for  $n = 3, 4, 5, 6$ , etc., we obtain the following result:<sup>1)</sup>

$n$ :	$\sin^2\left(\frac{\pi}{n}\right)$	$\varepsilon$ : ( $PQ = \varepsilon \times PN$ )
3	0,7500	—2
4	0,5000	—1
5	0,3455	$-\frac{(3-\sqrt{5})}{2}$
6	0,2500	0
7	0,1882	0,2472
etc.	etc.	all $< 1$

<sup>1)</sup> The number 2 is of course valid here, as can immediately be seen from a simple figure.

From this it is obvious that besides the value  $n = 2$ , the possibility of which needs no further discussion, *only* the values  $n = 3$ , 4, and 6 fulfil the conditions mentioned above. No value greater than 6 is allowable, and  $n = 5$  is excluded because of the irrational value of the corresponding parameter. It appears therefore that in this respect also the space-lattice may be considered as a geometrical interpretation



105.  
Bravais' Fourteen Types of Space-lattices.

lattices, and at the same time simplify the deduction of them to a considerable degree.

It was Bravais<sup>1)</sup> who in 1848 solved the problem: what are all possible types of symmetrical space-lattices? — not only completely, but at the same time applied the theory successfully to various problems concerning the internal structure of crystals.

Bravais demonstrated, that there are only *fourteen* possible types of symmetrical space-lattices, the unit-cells of which are represented in *fig. 105*. Their symmetry corresponds to that of the *holohedral* classes of the seven well-known crystal-systems; for the *triclinic*

trical interpretation of a fact previously stated, and intrinsically identical with the significance of Haüy's law, namely: the restriction of the possible crystallographical axes (Chapter V).

§ 6. The restrictions to be made in the discussion of the possible symmetries of space-lattices, as following from the considerations in § 5, will of course diminish very appreciably the number of possible symmetrical space-

<sup>1)</sup> A. Bravais, Journ. de l'Ecole polyt. 19. 1. (1850); 20. 201. (1851); Etudes crystallographiques, Paris, (1866), p. 1—128; 101—287; L. Sohncke, Pogg. Ann. d. Phys. 132. 75. (1867).

system only an oblique parallelopiped cell being possible, for the *monoclinic* two kinds of cells, for the *rhombic* four, for the *trigonal* only one rhombohedral cell, for the *tetragonal* system two kinds of cells, for the *hexagonal* only an equilateral trigonal prism, of which six contiguous ones are shown in the figure, — and for the *cubic* system three kinds of cells. The cells of the rhombic, tetragonal and cubic system which have a point in the centre of the parallelopiped cells drawn in *fig. 105*, can be also chosen in such a way that no point lies within the cell; in the cubic system for instance, the elementary cell would then have an octahedral form, with a point at each corner of the octahedron, etc.

§ 7. In connection with this we shall at the same time draw attention to a fact which will appear of interest to us in future for the understanding of special groups of phenomena. It concerns the existence of so-called elements of *pseudo-symmetry* in such space-lattices, — a fact which finds its explanation in the special circumstance that there may exist a gradual passage of form from the one kind of unit-cell to the other.

Thus comparison of the elementary cells of both the tetragonal cells with the types *a* and *b* of the rhombic and the cubic system, will make it clear at once that a suitable change of the principal dimensions in one or two directions will make their form approach as closely as desired to that of a cubic cell. In the same way, if the dihedral angle of the oblique monoclinic cell, differing from  $90^\circ$ , approaches very closely to this value, the cell becomes almost that of a rhombic space-lattice.

When the principal ternary axis of the rhombohedral cell is suitably lengthened or shortened, the polar dihedral angles can approach to  $90^\circ$  as closely as possible, the rhombohedral cell being therefore converted almost into a cube. Indeed, the rhombohedron is a distorted cube, namely, if the latter be compressed or dilated in the direction of one of its four trigonal symmetry-axes.

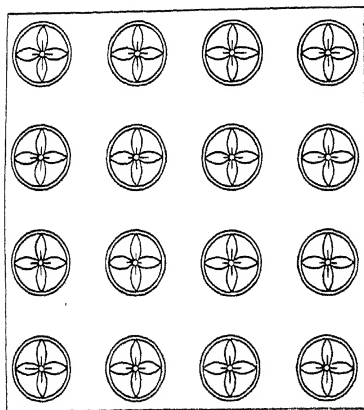
If the prism-angle of a rhombic prismatic cell be almost  $60^\circ$  or  $120^\circ$ , it approaches very closely to the equilateral triangular cell of the hexagonal space-lattice, etc.

In all such cases the lower symmetrical space-lattice exhibits a greater or smaller approximation to a space-lattice of higher symmetry. It is said to possess a *limiting* or *pseudo-symmetry*: the space-lattice is called *pseudo-cubic*, *pseudo-hexagonal*, etc., to indicate that, — although having truly a lower degree of symmetry, —



its dimensions and its whole character closely approach to those of a really cubic or hexagonal space-lattice. In the case of such a rhombic, but pseudo-trigonal or pseudo-hexagonal arrangement for instance, the vertical axis is of course only a binary axis of symmetry; but its direction is at the same time that of an *approximately ternary or senary* axis. The space-lattice is said to have an axis of *apparent symmetry*; and, as we shall see afterwards, such pseudo-ternary or pseudo-hexagonal axes, — although, properly speaking, being *no real* symmetry-elements of the space-lattice, — can occasionally have some of the functions of true symmetry-axes.

We will consider this fact more in detail in the next chapter of this book, in connection with some remarkable phenomena met with in crystalline matter.



106.

§ 8. For the moment we will return to our *two-dimensional* patterns of § 2, the character of which, as we have seen, is always closely related to a certain net-plane. Such pattern can eventually possess a certain symmetry, and the question may arise: what relations exist between the symmetry of the pattern and that of its characteristic net-plane?

In *fig. 106* and *107* two patterns are reproduced whose net-planes are essentially *identical*, namely a net-plane with ordinary *quadratic* meshes. This net-plane can therefore be considered as having an infinite number of quaternary axes perpendicular to the plane of drawing, and four sets of symmetry-planes passing through those axes; moreover their intersections with the plane of the figure are binary axes, and of course there is also an infinite number of symmetry-centres.

In *fig. 106* a repeat is placed round each point of the described net-plane, which has itself precisely *the same set of symmetry-elements*; in *fig. 107* however a motif is chosen in which only the quaternary axis has remained, while all other symmetry-elements of the quadratic net-plane are lacking in it. Now from these figures it can

immediately be seen that the pattern in *fig. 106* as a whole possesses just *the same* symmetry as its net-plane, while that in *fig. 107* has only a set of parallel quaternary axes perpendicular to the plane of the drawing. Such a pattern therefore appears to have at the best the symmetry of its own net-plane, namely if its repeat has exactly the same symmetry-elements which the net-plane possesses; but if the repeat has a *lower* symmetry than the net-plane has, the pattern as a whole must also exhibit a lower degree of symmetry, *possessing only those symmetry-elements which are common to its motif and its net-plane.*

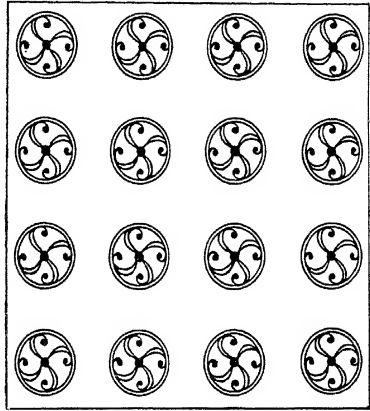


Fig. 107.

The same is true in the case in which a tridimensional space-lattice is considered, the points of which are substituted by stereometrical figures of a certain sym-

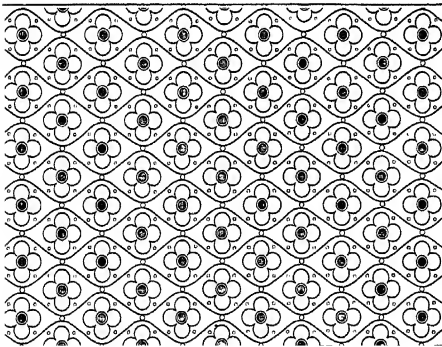


Fig. 108.

metry, playing the part of repeats for the tridimensional pattern resulting in this way. The pattern as a whole can never have a higher symmetry than its characteristic space-lattice has; but often its symmetry is appreciably lower, because its symmetry-elements

are only those, which its space-lattice and its motif have in common. Closer examination of *fig. 108* may soon give the conviction that also in the case where the motif of the pattern has a higher degree

of symmetry than its net-plane, the symmetry of the pattern as a whole nevertheless does *not* possess a higher symmetry than its net-plane has.

In *fig.* 108 the motif is tetragonal, the net-plane rhombic; and the pattern as a whole is rhombic also.

Bravais has made use of facts of this kind to explain the internal structure of crystals which belong to the *merohedral* classes of the seven crystal-systems. For, as we have seen, all the fourteen types of possible symmetrical space-lattices have the symmetries of the *holohedral* class of each system. If however round every point of these space-lattices molecules be placed, which only possess a certain part of the symmetry-properties characteristic of the space-lattice under consideration, the molecular structure as a whole can only exhibit the symmetry-elements which are common to the space-lattice and the complex crystal-molecules. And precisely because the space-lattice and its complex molecule still have some symmetry-elements in common, these molecules will all remain in *parallel* positions with respect to each other, in the same way as the repeats of *fig.* 106, as well as those of *fig.* 107 are parallel to each other. All homologous atoms of these complex molecules will therefore be arranged in similar and similarly oriented space-lattices, which can be brought to coincidence with each other by the characteristic symmetrical operations of the complex-molecule.

§ 9. It is evident however that the solution of the problem of homogeneous symmetrical arrangement as given by Bravais, cannot be considered the most general and thus not a final one, because the condition that all motifs of the stereometrical pattern shall be parallel to each other, is a quite arbitrary factor in it, and the deficiency of the theory in explaining the occurrence of lower symmetrical dispositions than those of the space-lattices, is only apparently eliminated by attributing to the motifs themselves such qualities as had to be explained by the principle of homogeneous symmetrical arrangement alone. With respect to the explanation of crystallographical phenomena, Bravais' supposition of the parallel orientation of all crystal-molecules appears more particularly untenable: the phenomena of twin-formation, and those concerning the homogeneous deformations along so-called "gliding-planes", prove the incorrectness of this hypothesis in a convincing way.

The more general solution of the problem: to deduce all possible homogeneous and symmetrical arrangements of equal

things, independent of their accidental qualities, was solved by Sohncke<sup>1</sup> for the cases in which only symmetry-properties of the first order were considered; afterwards the complete solution, including also the symmetry-properties of the second order, was given by Von Fedorow<sup>2</sup>) and bij Schoenflies<sup>3</sup>), while similar studies on the principle of homogeneity were published by Barlow<sup>4</sup>) and others<sup>5</sup>). Of course, as soon as tridimensional arrangements be considered, which have also symmetry-properties of the second order, the necessity arises of adopting the possibility in such systems of *two* kinds of "motifs" which are *enantiomorphous* with respect to each other. For by the operations of the second order characteristic for the tridimensional pattern, each motif is converted into its mirror-image; and as soon as the motif itself is deprived of all qualities, and therefore of all specific symmetry, its mirror-image must be in general non-superposable with itself.

Therefore homogeneous systems in space, possessing also symmetry-properties of the second order, must be built up by two enantiomorphously related kinds of repeats, and only such patterns as are themselves different from their mirror-images, i. e. which possess only symmetry-properties of the first order, are in general formed by the regular arrangement of one and the same kind of pattern-units.

The regular structures, as deduced by Sohncke, are completely determined by *rotations* and *translations*; the latter and their combinations with certain motions about axes of the first order, which

1) L. Sohncke, *Entwicklung einer Theorie der Krystallstruktur*, Leipzig, (1879); *Wied. Ann. der Physik.* **16**. 489. (1882); *Zeits. f. Kryst.* **13**. 214. (1888); **14**. 417, 426. (1888); *Pogg. Ann. d. Phys.* **137**. 177. (1869).

2) C. E. Von Fedorow, *Symmetrie der regelmässigen Systeme von Figuren* (1890); *Zeits. f. Kryst.* **20**. 25. (1892); **24**. 209. (1895); **25**. 113. (1896); **28**. 232, 468. (1898); **31**. 17. (1900); **36**. 209. (1902); **37**. 22. (1903); **38**. 322. (1904); **40**. 529. (1905); **41**. 478. (1906).

3) A. Schoenflies, *Krystallsysteme und Krystallstruktur*, Leipzig 1891), p. 237; *Zeits. f. Kryst.* **20**. 359. (1892); **54**. 545. (1915); **55**. 323. (1916).

4) W. Barlow, *Nature* **29**. 106, 205. (1883); *Chem. News*, **53**. 3, 16. *Zeits. f. Kryst.* **23**. 1. (1896); **25**. 86. (1897); **27**. 449. (1897); **29**. 433. (1899).

5) L. Wulff, *Zeits. f. Kryst.* **13**. 503. (1888); **14**. 552. (1888); E. Blasius, *Ber. d. bayr. Akad. d. Wiss. München* **19**. 47. (1889); *Zeits. f. Kryst.* **19**. 512. (1892); C. Viola, *ibid.* **31**. 114. (1900); **35**. 229. (1902); **41**. 521. (1906); A. Nold, *ibid.* **40**. 13, 433. (1905); **41**. 529. (1906); **48**. 321. (1911); F. Haag, *Zeits. f. Kryst.* **14**. 501. (1888); K. Rohn, *ibid.* **35**. 183. (1902); J. Beckenkamp, *Zeits. f. Kryst.* **44**. 576. (1908); **45**. 225. (1908); **47**. 35. (1910); E. Riecke, *Zeits. f. Kryst.* **36**. 283. (1902).

represent therefore *helical* motions, — are indeed operations of essential significance for unlimited systems, as we have seen in Chapter II.

Owing to the fact that in these unlimited systems there are sets of parallel axes of rotation or helicoidal motion, it is of interest to point here again to the fact that the simultaneous existence of such parallel axes involves always the existence of others, which can be found by the construction of Euler (see Chapter III, p. 28). Some examples may make this clear.

Let (*fig. 109*)  $A_1$  and  $A_2$  be two parallel quaternary axes. If we apply Euler's construction to find the resulting axis, we must realise that the centre of the sphere used in *fig. 18* is now at infinite distance, the surface of the sphere therefore being changed into a plane perpendicular to  $A_1$  and  $A_2$ , and thus coinciding with the

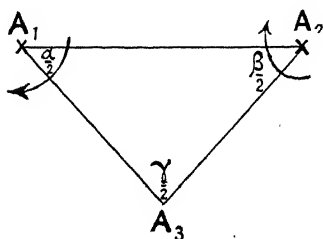


Fig. 109.

plane of our drawing here. When the rotations are both clockwise, we must construct the

angles  $\frac{\alpha}{2} = \frac{\beta}{2} (= 45^\circ)$  as indicated in the figure, and because

$\angle A_1 A_3 A_2 = 90^\circ$  therefore, it appears that  $A_3$  is a *binary* axis ( $\gamma = 180^\circ$ ), parallel to  $A_1$  and  $A_2$ . Indeed, the existence of

such parallel binary axes, as a necessary consequence of the presence of  $A_1$  and  $A_2$ , is confirmed for instance in the patterns of *fig. 106*, *107*, *112*, etc.; the arrangement of the quaternary axes of the pattern appears the same as that of the alternating binary axes. In the same way it is seen from *fig. 113*, that the senary axes alternate with sets of ternary and of binary axes there, which follow from the simultaneous presence of the parallel senary axes in exactly the same way.

If, however, the rotations round  $A_1$  and  $A_2$  had *opposite* directions, so that the algebraic sum of their angles of rotation were  $= 0$ , the axis  $A_3$  would be situated at an infinite distance; the result would therefore be a *translation*. From *fig. 110*, which show the successive rotations round  $A_1$  and  $A_2$  over angles  $\alpha$  and  $-\alpha$ , which are together equivalent to a translation  $A_1 A'_1$ , it is easily seen that the dimension of this translation is  $2 A_1 A_2 \sin \left( \frac{\alpha}{4} \right)$ .

A detailed study teaches moreover that the combination of

axes of helicoidal motion in such infinite systems is governed by exactly the same laws, as were previously found in the case of the combination of ordinary axes of rotation: in general we can deal with such helicoidal axes in just the same way as if they were mere axes of rotation: the periods of the helicoidal axes possible in infinite systems, can also be no other than we found for the axes of simple rotation.

If rotations or helicoidal motions be combined with a translation  $t$  perpendicular to the axis under consideration, it can be easily demonstrated (*fig. III*) that the result of this is always

a motion about another axis parallel to the first. Let  $A_1$  (*fig. III*)

be an axis of rotation or of helicoidal motion, and let  $t$  be the characteristic translation perpendicular to that axis. A point  $P_1$  of the system arrives at  $P_2$  by the rotation through an angle  $\alpha$  round the axis  $A_1$ , or in  $P'_2$  situated above the plane of rotation, if  $A_1$  be a helicoidal axis. Because  $P_1$  and  $P_2$  are two points of the system nearest to each other,  $P_1P_2$  is a characteristic translation of it, and as  $t$  has the same function,  $P_1$  can always be chosen in such a way that  $P_1P_2$  is parallel and equal to  $t$ ; this is the case represented in *fig. III*.

Now this translation brings  $P_2$  back in  $P_1$ , and makes  $A_1$  coincide with a similar axis  $A'_1$ . Therefore the combination of both motions is equivalent to a rotation about an axis passing through  $P_1$ , which brings  $A_1$  into  $A'_1$ ; and the angle

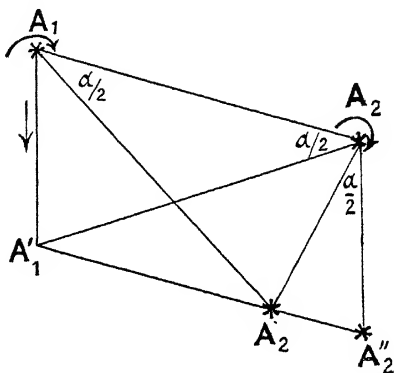


Fig. 110.

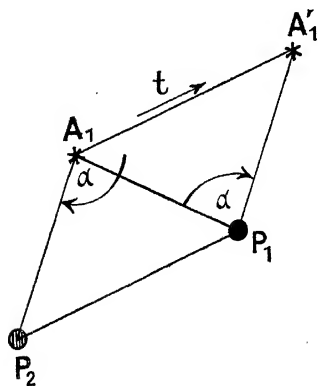


Fig. 111.

of rotation of the axis passing through  $P_1$  must therefore also be  $\alpha$ .

The axis resulting from the simultaneous existence of the translation  $t$  and the rotation about  $A_1$ , is evidently situated normally with respect to the rotation-plane of  $A_1$ , and in the top of an isosceles triangle which has  $t$  as its base, and  $\alpha$  as its top-angle; the top lies at that side of  $t$  in the direction of which the rotation round  $A_1$  occurs.

§ 10. These instances may be sufficient to give at least some impression of the way in which different motions in such infinite systems will determine others, if combined with each other.

In chapter *II* we have indicated how the symmetry-properties of such systems can be generally deduced by the method of Boldyrew,

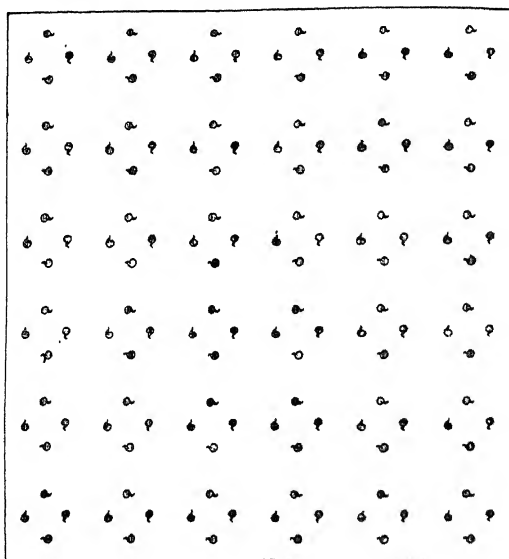


Fig. 112.

and others. The systematical deduction of all possible symmetrical arrangements, being a purely mathematical and very extensive problem, may also therefore be omitted here, and only some general properties of these systems be elucidated by suitably chosen examples.

Most of the *sixty-five* Sohnckian systems can be imagined to be deduced from the space-lattices of Bravais by replacing each point of them by definite, similarly composed, groups of points, the symmetry-elements of which are however differently oriented with

respect to those of the fundamental space-lattice. In *fig. 112* a section through such a system is reproduced, the points of it being replaced by absolutely unsymmetrical repeats. The existence of an infinite number of tetragonal axes and of an infinite number of binary axes situated between them, and arranged in the same disposition, is clearly exhibited by the pattern, and also the existence of central symmetry. Moreover the characteristic translations of the fundamental net-plane of the pattern, are easily recognisable.

Something analogous occurs in the regular system, a section of which is represented in *fig. 113*.

Here a set of parallel senary axes *A* is present, while trigonal axes *B* and digonal axes *C* alternate with them, in accordance with Euler's theorem. If the hexagonal cells be reduced to a single point, there results an arrangement which is not different from the hexagonal space-lattice of Bravais; but when the hexagons extend and reach

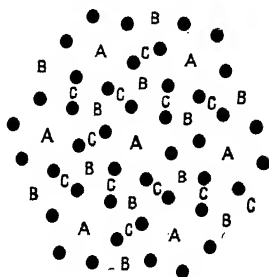


Fig. 113.

their neighbours, the result will be an arrangement, a section of which is reproduced in *fig. 114*, and which is evidently not met with amongst the regular systems deduced by Bravais.

Generally speaking, the Sohnckian systems can be considered to be built up from *n* congruent and parallel interpenetrating space-

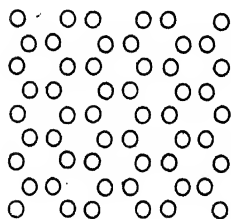


Fig. 114.

lattices of Bravais. The repeats placed in the various points of the same space-lattice are all parallel to each other; they are however not similarly oriented in the different composing space-lattices, but they can be brought to successive coincidence with each other by the characteristic motions of the regular system under consideration. An observer placed in the consecutive non-parallel motifs of the pattern, will then see the whole infinite system always

in the same way, only when he subjects himself to the successive symmetrical operations characteristic of each group of non-parallel motifs; for instance in *fig. 112*, if he looks every time in the direction of a quaternary axis of each tetrad of motifs.



In *fig. 115* two non-superposable regular systems are reproduced in projection, which are characterised by a set of parallel trigonal screw-axes perpendicular to the plane of the figures; their points are substituted by perfectly asymmetrical repeats. The repeats of three consecutive layers are distinguished by their colour, and they are tinted more darkly, the nearer they are to the observer's eye. It is obvious that we have here two arrangements, characterised by right and lefthanded screw-axes, and being real non-superposable mirror-images of each other. Crystals whose unsymmetrical molecules were placed in the points of these regular systems, would evidently exhibit true *enantiomorphism*, as for instance is often observed in the case of crystalline substances endowed with optical rotatory power.

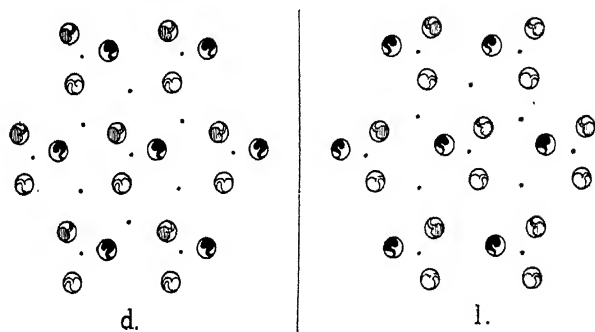


Fig. 115.

§ 11. With respect to the symmetry of Sohncke's sixty-five regular systems, we may remark here that they are all characterised by rotations and translations, and that their symmetry is exactly the same as that of the symmetry-groups previously deduced, possessing only symmetry-properties of the first order. If the points in these regular systems be substituted by absolutely arbitrary repeats, the symmetry of the resulting pattern will *not* be influenced by the specific geometrical nature of these repeats, if the latter only be all identical and placed in an analogous way with respect to the axes of the system.

But if these patterns should also have symmetry-properties of the second order, e.g. a central symmetry or symmetry-planes, then again special symmetry-properties of this kind must be attributed to the motifs themselves, just as appeared to be the case in Bravais' explanation of the lower symmetrical crystal-forms.

Sohncke's theory shows therefore in *this* respect an analogous deficiency to that of Bravais, if used for the explanation of such higher symmetrical crystal-structures, although its deficiency has another significance, and is not so strongly marked, as that of Bravais' view. Therefore Sohncke's theory must certainly be considered to be a real progress in comparison with that of the latter, although the problem mentioned above has evidently not yet got its most general solution by it.

§ 12. Before finishing these considerations of Sohncke's regular systems, we may remark here that the theory can be extended also to cases in which the constitutive repeats of the tridimensional pattern are no longer of the same kind, but of *different* character. If a definite number of such Sohnckian systems, which all possess the same and parallel translations, but which are neither congruent nor need be built up by the same particles, be suitably placed the one into the other, such an interpenetration can lead to a complex, materially heterogeneous system, the foundation of which is a space-lattice which is characterised by the translations just mentioned.

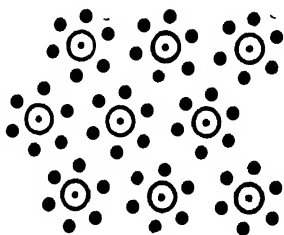


Fig. 116.

As an instance of this, a section of such a periodical pattern has been represented in *fig. 116*. It is deduced from the pattern of *fig. 113* in such a way that a motif of an other kind is placed every time at the centre of each hexagonal group of *fig. 113*. The fundamental features of the regular systems are evidently preserved in this new arrangement too, and Sohncke has, for instance, proposed systems of this kind to explain the crystal-structure of complex molecular compounds like salt-hydrates, etc. Moreover he was able to give a rational explanation in this way of the occurrence of some *tetartohedral* and *hemimorphic* crystals, which could not be explained by means of the original, unextended theory of his.

Another example of two such interpenetrating systems built up from two different motifs, is the pattern shown in *fig. 117*. Here the symmetry of the whole pattern is evidently the same as of each of its motifs, these having the same tetragonal symmetry.

The extended theory of Sohncke can be used successfully for the explanation of the structure of crystalline chemical compounds,

if it be supposed that the points of all interpenetrating space-lattices of such a system are replaced by one and the same kind of chemical atoms; to this we will draw attention again later on.

§ 13. However from the above it may be clearly seen that the application of the theories of Bravais and Sohncke to the problems of crystal-

structure, always involves to a certain degree certain suppositions about the special properties of the molecules which take the places of the points in the deduced arrangements.

From a mathematical viewpoint however it is of importance to solve the problem: how to find the total number of such arrangements of re-

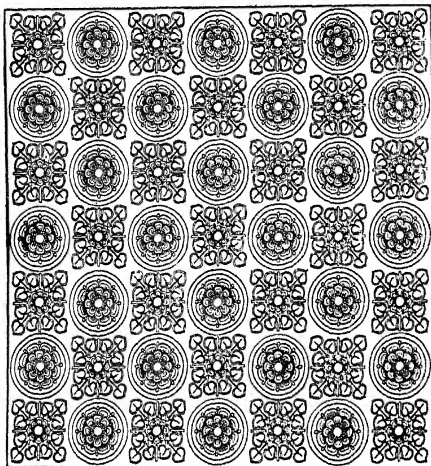


Fig. 117.

peats that the tridimensional patterns produced may have all the 32 symmetries which are possible for stereometrical regular systems, without it being necessary to make any special assumption about the nature of the constituent motifs. As we have seen (§ 9), the solution of this problem involves the supposition of two enantiomorphously related repeats, as soon as there is question of patterns having symmetry-properties of the second order.

The mathematical problem just mentioned has been solved by Von Fedorow and by Schoenflies<sup>1)</sup>; and although it would be quite out of place here to give a full account of these deductions, some general remarks as to the way followed by these authors may be of interest.

Both authors subdivide the unlimited space into an infinite number of equal or enantiomorphously related, contiguous small volumes

<sup>1)</sup> loco cit.; see also: A. Schoenflies, *Zeits. f. Kryst.* **54**, 545. (1915); **55**, 323. (1916); F. Wallerant, *Bull. de la Soc. Miner.* **21**, 197. (1898).

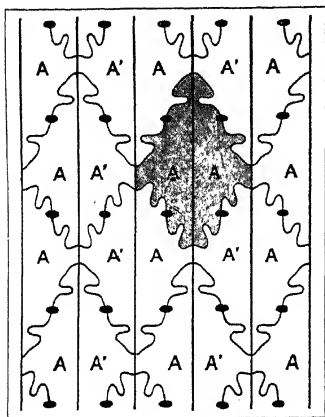
filling up that space completely. The distribution of matter within such an elementary volume, — which Von Fedorow calls a *sterohedron*, while Schoenflies prefers the name of *fundamental domain* for it, — is supposed to be completely arbitrary and free from all symmetry. Its volume is constant and equal to that of the elementary parallelepipedon of the space-lattice, or a multiple of it. When some of these identical or enantiomorphous "fundamental domains" in symmetrical space-lattices or structures, are eventually combined into greater units exhibiting a certain symmetry, these symmetrical "complex domains" which by similar repetition are also filling up the whole space, are discriminated by Von Fedorow as *parallelohedra*<sup>1)</sup>. Corresponding points of such parallelohedra are also corresponding (homologous) points of the regular system, and they are always arranged in a space-lattice characterised by a definite group of translations, etc.

It is easy to demonstrate, moreover, that *no* existing symmetry-elements can ever lie *within* the fundamental domain of a regular structure, but that they are always situated on its *surface*. This follows immediately from the fact that each symmetrical operation must always bring a fundamental domain into coincidence with *another* one present in the whole complex. From this it is clear that the existence of symmetry-axes and of symmetry-planes in the structure will then of course be in some way determinative for the shape of the fundamental domain, as e. g. symmetry-planes must be always limiting parts of the surface of such fundamental cells (*fig. 118*). In the latter cases it also becomes clear that in general to every fundamental domain *A*, a second one *A'*, being the *mirror-*

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1) If a point of a space-lattice be joined with all *nearest* points situated round it, and planes perpendicular to the midst of these lines be constructed, a volume of space is separated which is limited by fourteen planes which are pairwise parallel to each other. In a cubic space-lattice for instance these planes are perpendicular to the edges of the cubic cell and to the four cube-diagonals. The „fundamental domain” thus determined, — a *hepta-parallelohedron*, — is in the latter case a cube, the corners of which are truncated by planes of the octahedron. With elements of this shape space can be filled without any room remaining between the composing cells. These *hepta-parallelohedra*, already used by Lord Kelvin, have an important share in the deductions of Von Fedorow. However, it may be remarked here that it is not necessary to determine the special shape of the fundamental domain. This form can be quite arbitrary; but its volume is always constant and equal to that of the elementary cell of the space-lattice, or in regular systems in general a multiple of this.

image of the first, must be present, because the reflection of the elementary volume  $A$  in the symmetry-plane will change it into its contiguous, but in general non-superposable mirror-image  $A'$ , etc. Within all such enantiomorphously related fundamental domains the whole distribution of matter must of course also be enantio-



118.

morphous; and this is the meaning of the supposition of Von Fedorow and Schoenflies, when they maintain that crystals possessing symmetry-properties of the second order must be built up by certain atom-complexes (crystal-molecules) which are of *two*, enantiomorphously related, kinds. Only in the cases of enantiomorphous crystals the righthanded and lefthanded crystals can separately be composed by atom-complexes of one and the same kind, right *or* lefthanded. If such crystals as,

for instance, those of dextro- and laevogyrate *sodium-chlorate*, are dissolved, giving an optically *inactive* solution, the supposition must necessarily be made that a re-arrangement of the atoms during the process of dissolution takes place, producing an equal number of both kinds of enantiomorphous molecules, or perhaps a quite different species of them, superposable with their mirror-image. This is intimately connected with the fact that the notion of the fundamental domain is a purely mathematical one, and therefore with respect to the endless periodical repetition of equal parts throughout the regular structure, the gathering together of certain atoms into complexes, is within wider limits a quite arbitrary, purely mathematical fiction. The notion of "molecular complex" is in the crystalline state therefore *formally* without significance; which however does *not* mean that the connections between the constituting atoms, as involved in the study of the properties of the *chemical* molecule, should have completely disappeared (See p. 153). Only they need not be considered for the mathematical description of the crystalline,

periodical arrangement; that is all. The specific character of the crystal-structure lies in the fact that all atoms of the same kind are equivalent for the architecture of the crystal, and that for the mechanical equilibrium finally reached therein, the total action of each atom is as if it were an autonomous individual. Atoms of different kinds can moreover always be grouped together so as to form complexes which, similarly and infinitely repeated in an absolutely regular and periodical way, according to the special symmetry-properties of the whole structure, will fill up space to produce the remarkable masterpiece of nature, that we call a crystal.

However it is exactly this very general character of the theory which makes its application to concrete cases rather difficult. The whole number of symmetrical arrangements thus found amounts to no less than *two hundred and thirty*, the symmetry of which can be grouped in the same 32 classes as we have previously found to be possible for crystals (Chapter V).

A considerable number of possible structures belongs therefore to each of these 32 classes; and as for the explanation of physical phenomena the precise arrangement of the constitutive atoms is the point of interest which this general theory leaves totally out of consideration, the chance of its successful application for the purpose of explaining crystallographical and crystallophysical phenomena cannot be said to be very hopeful. But this general and, from a mathematical point of view, highly finished theory certainly remains of interest, as being the final and exhaustive solution of the special mathematical problem concerning the regular arrangement in discontinuous and homogeneous systems.

**§ 14.** In the preceding paragraphs we repeatedly had occasion to point out that the most general properties of space-lattices and of regular structures, were just those, by which also crystals are characterised. Crystalline matter behaves in many respects as a physical medium of continuous structure; but for a number of physical phenomena, as for instance with respect to its *cohesion*-, and *growth*-phenomena, with respect to its influence on a thin pencil of Röntgen-rays travelling through it, etc., it exhibits an undeniable *discontinuous* character. The validity of Haüy's law for space-lattices, the correspondence of the values for the periods of eventually occurring symmetry-axes in regular systems of the kinds mentioned above, and the circumstance that all possible regular structures as deduced in the modern structure-theories belong exactly to the same 32 classes to which

also crystals may be reckoned, — are all facts which give the conviction that an explanation of crystallonomical phenomena, presupposing an analogous internal structure for crystals such as those dealt with in the above, will certainly be successful.

It was precisely for this purpose that in the middle of the nineteenth century Bravais began his famous studies on space-lattices.

With great acumen and in a most ingenious way he really developed these views gradually for the explanation of the most important properties of crystalline substances; later on his methods were followed with admirable success especially by French authors, for the explanation of a great number of physical phenomena, and it cannot be denied that Bravais' simpler and more transparent ideas have been far more effectual for the development of the science of crystalline matter, than those concerning the more general, but incomparably more complicated regular arrangements of Sohncke, Von Fedorow and Schoenflies. Another cause of this is also the particular fact that up till now there had been no method available which allowed in any concrete case of making a definite choice between the numerous structures possible in the same crystal-class. In most cases it remained therefore merely a question of personal preference, which grouping of particles an observer wished to attribute to the crystal-species under investigation; and it is conceivable that under such conditions most crystallographers felt inclined rather to adopt the simpler views of Bravais, than the much more complicated doctrine of the regular arrangements in space, discussed in the above <sup>1)</sup>.

§ 15. The problem of giving a rational deduction of the crystalline structure from the chemical composition of the crystal has puzzled investigators ever since early times. It has been more in particular the deduction of the observed *symmetry* which originally occupied most workers in this field, and in this respect the endeavours of Groth <sup>2)</sup> in 1870 are worthy to be remembered, who tried

<sup>1)</sup> Cf. also: G. Friedel, Bull. de la Soc. Minér. **31**. 326. (1907); G. W. Wulff, Zeits. f. Kryst. **47**. 607. (1910).

W. J. Sollas, Proc. Royal Soc. **63**. 270. (1898); **67**. 493. (1900); **69**. 294. (1902); **80**. A. 267. (1908); Brit. Assoc. Rep. (1907), p. 481.

G. Cesàro, Bull. Acad. R. belge, (1901), p. 303; P. Groth, Zeits. f. Kryst. **54**. 65, 498. (1914); E. Riecke, Phys. Zeits. (1900). *I*. 277; Ann. der Phys. **3**. 545. (1900).

<sup>2)</sup> P. Groth, Ber. d. d. Chem. Ges. **3**. 449. (1870).

to find out what change the symmetry of the crystalline substance undergoes when one of its *hydrogen*-atoms is replaced by another univalent atom or radical. The phenomena observed in such cases are named *morphotropism*.

Some frequently occurring facts could be stated in these investigations, although it appeared impossible to find here absolute regularities, because it very soon became clear that the "morphotropic action" of any substitute does not only depend on its proper chemical character, but also on that of the substituted molecule.

Thus Groth was able to draw attention to the fact that the substitution of a *hydrogen*-atom in organic molecules by a *hydroxyl*- or *nitro*-group, has commonly as a consequence only a rather slight and one-sided change of the crystallographical parameters of the substituted substance, while the original symmetry of it is usually preserved. The substitution of *hydrogen*-atoms in such molecules by *halogen*-atoms or by *alkyl*-groups, is however in almost all cases followed by a striking change of the crystallographical symmetry of the original substance. These rules are valid in most cases, but the number of exceptions is by no means negligible.

Other observers tried to trace the connection between chemical constitution and crystallographical symmetry by the comparative study of the crystal-forms of position-isomerides. The present author found in this way for instance<sup>1)</sup> that, although close relations between such position-isomerides are in general rather rare, in the case of 1-2-4-6-, and 1-2-3-5-*tribromo-toluenes* a complete *isomorphism* occurs, which is preserved in the corresponding *dinitro*-derivatives of them also.

Although no general rules concerning the relation between chemical composition and the degree of crystallonomical symmetry have hitherto been found, these, and an exceedingly great number of other phenomena, must convince us of the truth that a rational connection between crystalline form and molecular composition beyond all doubt exists. The discovery of *isomorphism* by Mitscherlich was a first step on the way towards the solution of the problem indicated above, as here the "analogy" in chemical composition is expressively pointed to. Isomorphism however is only a special case of the much wider conception of morphotropism, i. e. of the

<sup>1)</sup> F. M. Jaeger, *Kristallografische en Moleculaire Symmetrie van Plaatsings-isomere Benzolderivaten*, Dissertatie Leiden, (1903); *Zeits. f. Kryst.* **38**. 555. (1904); **39**. 170. (1904); **40**. 357. (1905).



causal relations between chemical and crystallographical arrangement and between the forces which determine the configuration of atoms in space, in connection with those governing the structural arrangement of the crystallonomical units.

§ 16. A highly suggestive theory concerning the problem mentioned, was developed in 1916 by Barlow and Pope <sup>1)</sup>. It represents a happy completion of Barlow's views on homogeneous configurations and the most closely packing of spheres by the aid of a new fundamental hypothesis about the relation between the valency of an atom and the space it occupies in such homogeneous assemblages. The domain of each chemical atom is a distinct portion of space, which it occupies by virtue of an influence exerted uniformly in every direction. These spheres of influence are now supposed to have a volume which in every compound is *nearly proportional to the valency of the atom*, the factor of proportionality being the same for all atoms of the same crystallised substance; and according to the authors, a crystalline structure must be regarded as *a most closely packed, homogeneous assemblage of the spheres of influence of the component atoms*.

The whole assemblage of atoms, most closely packed in the way described, is of course homogeneously partitionable into exactly similar cells which all contain a single chemical molecule.

It will be clear that each point in every cell corresponds to a homologous point in any other cell, and that these homologous points of the same kind will represent a space-lattice characterised by definite translations, and occasionally by definite rotations too.

The unit-cell containing the single molecule, and built up by spheres of atomic influence, has therefore in the whole assemblage a similar function as the "repeat" had in our "patterns" formerly discussed. The homogeneous, *periodical* nature of the whole structure makes the partitioning into "molecular cells" to some extent arbitrary from a theoretical point of view, just as was previously pointed out when we spoke of the significance of the conception of "molecule" in the crystalline state.

If a sphere be taken from the whole complex and replaced by

<sup>1)</sup> W. Barlow and W. J. Pope, Journ. Chem. Soc. London **89**. 1675. (1906); G. Le Bas, *ibid.* **91**. 112. (1907); W. Barlow and W. J. Pope, Journ. Chem. Soc. **91**. 1150. (1907); **93**. 1528. (1908); F. M. Jaeger, Zeits. f. Kryst. **44**. 61. (1907); W. Barlow and W. J. Pope, Journ. Chem. Soc. **97**. 2308. (1910); W. Barlow, Miner. Mag. **17**. 314. (1916); cf. also: W. Barlow, Zeits. f. Kryst. **29**. 433. (1889); cf. also the work of A. E. H. Tutton: Isomorphism and Crystal-structure, (1913).

another, the total solid volume of the replacing and replaced spheres must be almost the same. Thus the cavity produced by three *hydrogen*-atoms may be nearly filled up by one trivalent *nitrogen*-atom, etc.

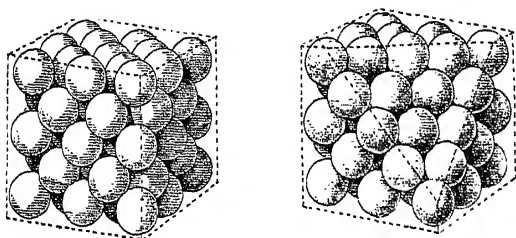
It must here be remarked that the proportionality of the volume of the influence-spheres and the valencies of the respective atoms, is only an *approximate* one. This follows among other things from the fact that the isomorphous substitution of *K* by *Rb*, or by *Cs*, does *not* lead to *identical* crystal-forms, and also from the fact that the univalent *Li*-, or *Na*-atoms do *not* replace those of *K*, *Rb*, *Cs*, isomorphously. From this the possibility of a slight shifting of these spheres in most closely packing after such substitutions, and, as a consequence of this, a change of symmetry, may be conceivable.

§ 17. The theory just described in outlines, has been applied by both the authors in a very ingenious way to explain a number of peculiarities and phenomena observed in crystals. For these applications we must refer the reader here to the series of publications mentioned in the preceding paragraph. It cannot be denied that there often appears some arbitrariness with respect to the way in which these assemblages are brought into agreement with the crystallographical data at hand, especially with respect to the selection of the "multiples of the axial ratios" as calculated from direct measurements. This is the same criticism which has often been actually made of analogous trials made by other investigators to elucidate relationships between crystalline forms of different, but closely related substances. Multiplication of axial ratios with other numbers than those following from the directly observed Millerian indices of the occurring crystal-facets, with the purpose of bringing out analogies in form with the crystal-forms of other substances, is a dangerous process. By suitable choice of the multipliers, all desired axial ratios can finally be made comparable with each other. Notwithstanding this, it can be seen from the Barlow-Pope-theory that a certain persistence of a particular type of structure as an element throughout widely differing assemblages, often occurs in the case of substances which are substitution-products of a same mother-compound; and also, that the structures of two polymorphous modifications of a same substance are often very simply related to each other.

It is of no use to study all the cases considered by the authors in the light of these conceptions, nor to mention all the numerous conclusions to which they have arrived, because, as we shall see

afterwards, the results to which they have come differ in many respects appreciably from those obtained by means of the more objective diffraction-method of Bragg, and because further research must therefore bring full evidence as to the correctness of the one view or the other. But it may be of interest to say some few words about the crystalline forms of the *chemical elements* as seen from this standpoint, and of some simply constituted oxides of bi-valent metals also. We are namely here dealing with the relatively simple case of the symmetrical marshalling of *equal* spheres. These considerations may be useful afterwards also from another point of view.

§ 18. It is a well-known fact that the *elements* crystallise in



*a.*

Fig. 119.

*b.*

Cubic Assemblage of Equal Spheres.

either the cubic or the hexagonal (ditrigonal) system. Assuming this phenomenon to have some relation to the hypothesis mentioned above, the question may arise whether the crystalline structures of these elements may be considered as most closely packed assemblages of *equal* spheres?

Equal spheres can be packed most closely under a general pressure so as to produce a completely homogeneous system in *two* ways only, which can be differentiated as the *cubic* and the *hexagonal* close-packed arrangements of equal spheres.<sup>1)</sup>

The *cubic* (tetrahedral) arrangement will be clear from *fig. 119 a* and *b*. It has all symmetry-elements of the *holohedral* class of the cubic system ( $K^H$ ). The centres of the spheres, the points of contact between the spheres, and the centres of the octahedral

<sup>1)</sup> W. Barlow, *Nature* **29**, 186. (1883); Lord Kelvin, *Proceed. Roy. Soc. of Edinburgh* **16**, 693. (1889).

groups of spheres shown in the octahedral section of *fig. 119b*, are all centres of symmetry of the unlimited system. The ternary axes are perpendicular to the planes of most closely packing of spheres in the whole system, and of these planes, which are parallel to those of the octahedron there are three consecutive ones differently arranged, the fourth being identical with the first and the seventh, the fifth with the second and the eighth, etc. (*fig. 119b*). The projection of three consecutive layers parallel to (111) is shown in *fig. 122*, and can make clear the mutual marshalling of the spheres in this direction if compared with the figure *121*, which in its turn represents the most closely packed assemblage of equal spheres mentioned above under the name of the *hexagonal* arrangement.

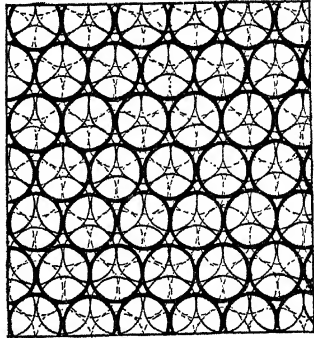


Fig. 120.  
Section parallel to (111).

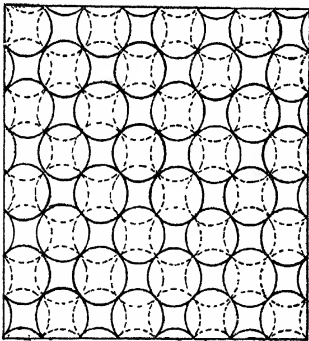


Fig. 121.  
Section parallel to (100).

The symmetry-elements of this hexagonal assemblage are those of the *holohedral* class of the hexagonal system. The system of spheres possesses parallel planes of symmetry passing through the centres of the spheres of each of its most closely packed triangularly arranged layers. (*fig. 122*). In the centres of the cavities of each triad of spheres, ternary axes of rotation are present perpendicular to the different layers just mentioned, in such a way that they pass simul-

taneously through a sphere-centre of an adjacent layer *b* and *c*; while through the centres of the cavities of every group of six contiguous spheres of two consecutive layers, senary screw-axes pass, of

course being also perpendicular to the symmetry-planes mentioned above.

The screw-axes do *not* pass through any sphere-centres at all; but three planes of symmetry pass through every senary screw-axis and through the centres of the three nearest spheres of consecutive layers. Three double sets of binary axes lie in planes midway between the layers of most closely packed triangularly arranged spheres, and perpendicular to the last described symmetry-planes, and they intersect

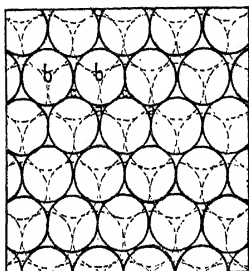


Fig. 122.  
Hexagonal Assemblage of Equal  
Spheres.

the senary screw-axes. Through every pair of nearest senary screw-axes a plane of "gliding" symmetry can be brought, which planes are evidently perpendicular to the binary axes just mentioned. In planes midway between the consecutive layers, the symmetry-centres of the endless system are situated on every senary screw-axis and at points midway between them. If the value of the *translation* perpendicular to each layer, by which a sphere of the first layer can be brought to coincidence with a superposed sphere

of the third layer, be taken as the *parameter* of the *c*-axis, while the distance of two contiguous spheres in each layer is taken as *a*-axis, — it will be obvious that the axial ratio of this hexagonal arrangement is:  $a : c = 1 : 2 \sqrt{\frac{2}{3}} = 1 : 1,6330$ , or half of it,  $= 1 : 0,8165$ . This value is therefore descriptive <sup>1)</sup> of such most closely packed hexagonal assemblages of equal spheres.

First now, there are a number of *chemical elements* which crystallise in the *cubic* system: *silver*, *mercury*, *gold*, *copper*, several *platinum* metals, etc., are well-known examples of this.

Secondly, a number of elements are *hexagonal*: *magnesium*, *beryllium*, *arsenic*, etc., may be mentioned among others. Moreover in cases of dimorphism of such elements, the change of *cubic* into *hexagonal* symmetry, and vice-versa, is frequently observed.

However the agreement of the axial ratios of these elements with

<sup>1)</sup> If however the perpendicular to the now adopted *a*-axis were chosen as such, the ratio:  $a : c = 1 : \sqrt{2} = 1 : 1,4142$  would have been the descriptive value for this assemblage, which of course is *equally* appropriate for the purpose of characterising the hexagonal assemblage under consideration.

both theoretical values, appears to be only an approximate one: for *magnesium* it is: 1 : 1,6242; for *beryllium*: 1 : 1,5802; for *arsenic*: 1 : 1,4025, while for most of them those values oscillate round 1 : 1,33.

The agreement is better in the case of the *oxides* and *sulphides* of *bivalent elements* as *zinc*, *cadmium*, *beryllium*. etc., where evidently the same conditions must exist. A few examples will make this clear <sup>1)</sup>:

<i>Zinc-oxide</i> . . . . .	$a : c = 1 : 1,6077.$
<i>Zinc-sulphide</i> . . . . .	$a : c = 1 : 0,8175$
<i>Beryllium-oxide</i> . . . . .	$a : c = 1 : 1,6305.$
<i>Cadmium-sulphide</i> . . . . .	$a : c = 1 : 0,8109.$
	etc.

§ 18. Notwithstanding this obvious, at least partial, agreement between measurements and calculations, we shall see that the structures following from the above mentioned theory agree only occasionally with the result of the recent investigations of some of these substances by means of Röntgen-rays. It will certainly therefore be necessary to postpone a final judgement of the various results obtained, until full certainty has been obtained about the real value of the conclusions drawn from the experimental results of the newly discovered methods.

There is however *one* point in which all these different investigators agree: it is the conviction of the soundness of the contention that constitutive atoms of a molecule preserve their individuality, and to some extent also their autonomy, as the component particles of a crystalline structure. The theory of Sohncke, that a crystal may be regarded as an interpenetration of regular point-systems, and the view maintained by Groth and by Barlow and Pope, that the structural units of these systems and space-lattices are the separate atoms of the chemical molecule, have been supported by modern experience, and their correctness seems to become more and more certain. It will therefore be of interest to consider these new methods of research here more in detail.

§ 20. In the preceding paragraphs we have learned to consider the crystal as a *discontinuous* system of atoms and molecules regu-

<sup>1)</sup> C. Friedel, Compt. rend. de l'Acad. d. Sciences Paris, **52**. 983. (1861); O. Mügge, Jahrb. f. Miner. **2**. 1. (1882); E. Mallard, Ann. des Mines, **12**. 427. (1887); H. Traube, Jahrb. f. Miner. Beil. Bnd. **9**. 147. (1894).

larly distributed in space, and elongated from each other by very small but definite distances. Physicists a long time ago made some evaluations of the order of magnitude of these inter-atomic and inter-molecular dimensions, which they found to be about  $10^{-8}$  or  $10^{-9}$  c.M.

Now it will be clear that an aggregation of particles of this kind will behave as a continuous body towards most physical agencies, because the dimensions which come into play in such physical phenomena, are commonly of an order of magnitude incomparably greater than the extremely small inter-atomic distances mentioned above. Thus, if for instance a pencil of visible light-rays travel through such a crystalline body, the latter will behave towards these vibrations like an anisotropous, but *continuous* medium, because the wave-lengths of the luminous vibrations vary from 0,00004 to 0,00007 c.M., this being about *ten thousand* times as great as the mutual distance between the consecutive particles of the assemblage.

From special phenomena observed with Röntgen-rays, suspicion had arisen among physicists, that the wave-length of these vibrations which seemed to have a close analogy to ordinary light-waves, should be extremely small, much smaller than those of the visible light. Diffraction-phenomena studied by Haga and Wind, afterwards by Walter and Pohl<sup>1)</sup>, and theoretical speculations by Wien, Stark, and others, had gradually led to the conviction that the wave-length of Röntgen-radiation would be of the order of  $10^{-8}$  or  $10^{-9}$  c.M. If this were true however, the wave-length would be of *the same* order of magnitude as the inter-atomic distances supposed in space-lattices of crystals, and in that case there would exist a great probability that the crystalline medium would behave *no* longer as a continuum towards Röntgen-radiation. It might be expected that the crystal would behave towards these extremely short transversal waves in a way analogous to that which the well-known "gratings" in optics do towards ordinary light-waves, and that a *diffraction*-phenomenon would occur, the nature of which would be analogous to that which would be produced when visible light fell upon a grating having *three* dimensions instead of only *two*.

§ 21. The ingenious idea that such a crystal might be used as

<sup>1)</sup> H. Haga and C. H. Wind, Wied. Ann. der Phys. (3). 68. 884. (1899); (4). 10. 305. (1903); B. Walter and R. Pohl, Ann. der Phys. (4). 28. 715. (1908); (4). 29. 331. (1909).

a tridimensional and most perfect "grating" for Röntgen-rays, was in 1912 conceived by Von Laue<sup>1)</sup>. The experiment was carried out in the spring of 1912 by Friedrich and Knipping<sup>2)</sup> in Sommerfeld's laboratory, and it was crowned with complete success. Round the central spot at the point where a thin pencil of Röntgen-rays, after passing the crystal, met the photographic plate, a great number of oval spots of different intensities were produced, which were symmetrically arranged about it, when the direction of the rays coincided with that of a symmetry-axis of the crystal-plate. In the preceding chapters some of these Röntgen-patterns have already been considered in detail, so that it is unnecessary here to dwell upon them.

Since then, an ever-increasing number of experimental and theoretical work has been published<sup>3)</sup> concerning this highly important phenomenon, which at the same time revealed the true nature of the Röntgen-radiation and created the possibility of studying the internal arrangement of the crystalline substances.

It proved not only the "transversal" nature of the Röntgen-radiation and made the determination of its wave-length possible, but it brought simultaneously the direct proof of the correct-

<sup>1)</sup> M. Von Laue, Bayr. Akad. d. Wiss. (1912), p. 303; Ann. d. Phys. **42**. 397. (1913).

<sup>2)</sup> M. Von Laue, W. Friedrich, and P. Knipping, Ber. Bayr. Akad. der Wiss. (1912), p. 303.

<sup>3)</sup> H. Haga and F. M. Jaeger, Proceed. Kon. Akad. van Wet. Amsterdam, Vol. **16**, **17**, **18**, (1914—1916); P. Debije, Verh. der phys. Ges. **15**. 678, 738, 857. (1913); P. P. Ewald, Sitz. kön. Bayr. Akad. d. Wiss. (1914) p. 325; Phys. Zeits. **15**. 399. (1914) P. P. Ewald and W. Friedrich, Ann. der Phys. **44**. 1183. (1914); W. H. and W. L. Bragg, Proceed. Cambr. Phil. Soc. **17**. 43. (1913); Proc. Royal Soc. London **89**. A. p. 277, 286, 477. (1913); Zeits. f. anorg. Chem. **90**. 153. (1914); G. C. W. Kaye, X-Rays, London, (1914), p. 168; W. H. and W. L. Bragg, X-Rays and Crystal-structure, London, (1915); E. Keller, Ann. der Physik **46**. 157. (1915); A. Johnsen Zeits. f. Kryst. **54**. 148. (1914); R. Glockner, Ann. d. Phys. **47**. 377. (1915); F. Rinne, Ber. d. math. phys. Klasse d. kön. Sachs. Ges. der Wiss. Leipzig, **67**. 303. (1915); **68**. 11. (1915); A. Sommerfeld, Münch. Med. Wochenschr. **42**. 1424. (1915); A. Johnsen, Centr. Bl. f. Miner. (1915), p. 331; P. Niggli, Ber. d. math. phys. Klasse der Sächs. Ges. der Wiss. Leipzig, **67**. 364. (1915); Zeits. f. anorg. Chem. **85**. 207. (1915); M. Von Laue, Ann. der Phys. **50**. 433. (1916); F. Rinne Zeits. f. anorg. Chem. **96**. 317. (1916); E. Wagner, Phys. Zeits. **14**. 1232. (1913); P. Pfeiffer, Zeits. f. anorg. Chem. **92**. 376. (1915); P. Debije and P. Scherrer, Nachr. d. Ges. d. Wiss. zu Göttingen, (1916), J. Olie and J. A. Bijl, (1917). Proceed. Kon. Akad. van Wet. Amsterdam, **19**. (1917).



ness of the ideas which crystallographers had already held for so long about the space-lattice-arrangement of the particles in the crystal.

Indeed, Von Laue showed that the problem could be attacked successfully on the basis of the ordinary diffraction-theory, the analytical treatment being however appreciably more complicated because of the *tridimensional* nature of the grating employed.

§ 22. For our purpose it is better, however, not to consider these

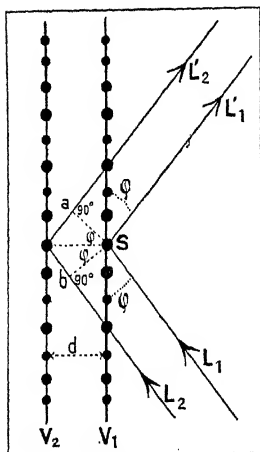


Fig. 123.

views in detail here, but to adopt an explanation of the phenomenon brought forward by W. L. and W. H. Bragg, which enables the questions considered here to be treated in a simple geometrical way and to avoid all calculations. It differs only from Von Laue's method in form, not in essence, as several authors have shown.<sup>1)</sup>

The principal idea of it is, that the phenomena observed can also be described *as if* the radiation were *reflected* by the consecutive parallel and equidistant molecular layers of the crystal under consideration, the "reflected" vibrations interfering with each other according to Huyghens' principle, because each particle becomes in its

turn the centre of a secondary wave-motion spread around it spherically, when a pulse of the incident beams passes over it.

Let us suppose, that the pencil of parallel Röntgen-rays  $L_1L_2$  (fig. 123) contains every possible wave-length over a wide range, its spectrum therefore being a continuous one. According to our suppositions, each atom of a net-plane  $V_1$  struck by the primary radiation, will become the centre of a new wavelet, and these various diffracted wavelets will touch a reflected wave-front perpendicular to the parallel beam  $L'_1L'_2$  which emerges from the crystal. The same will be true for the atoms of the consecutive net-planes  $V_2, V_3$ , etc.; but since the rays do not usually penetrate more than e. g. one

<sup>1)</sup> Cf. T. Terada, *Proceed. Tokyo math. phys. Soc.* 7. 60. (1913); G. W. Wulff, *Phys. Zeits.* 14. 217. (1913).

millimetre deep into the substance, it is only a relatively thin layer of crystalline substance that is engaged in the phenomenon considered, and in every case the number of "reflecting" net-planes is a finite one. Only when the reflected wave-trains are *in the same phase*, i. e. when they interfere with phase-differences of  $\lambda$  or a multiple of  $\lambda$ , an interference-maximum will occur. Now if  $bS$  be the plane perpendicular to the incident beam of radiation, and  $aS$  that perpendicular to the "reflected" beam  $L'_1 L'_2$ , the difference in the path travelled by a ray coming from  $V_1$ , and by that coming from  $V_2$ , will obviously be  $bP + Pa$ . But  $bP = Pa$ , is the projection of the distance  $d$  between two consecutive net-planes  $V_1$  and  $V_2$  upon the direction of the incident and emergent beam, and therefore equal to  $d \sin \phi$ , when  $\phi$  is the glancing angle which the incident pencil makes with the planes  $V_1$  or  $V_2$ . The whole phase-difference is therefore:  $2d \sin \phi$  and an interference-maximum will only occur, if this difference be equal to  $\lambda$ , or to a multiple of it:  $2\lambda, 3\lambda, 4\lambda$ , etc.

It is obvious that from the equation:

$$2d \sin \phi = n\lambda,$$

it follows that for constant  $d$  and for each definite value of  $\lambda$ , the angle  $\phi$  can only have definite values  $\phi_1, \phi_2, \phi_3$ , etc., the sines of which are *rational multiples* of each other. Conversely: if  $V_1$  be given in a certain crystal,  $d$  is wholly determined by the internal specific crystal-structure, and when homogeneous radiation of a known wave-length  $\lambda$  be used, we have only to measure  $\phi_1, \phi_2$ , etc., to find the distance  $d$  between two consecutive layers parallel to  $V_1$ . On the other hand it must be clear that from all wave-lengths present in the incident radiation, only that which is equal to  $\lambda$  will be reflected under the angles mentioned, when the plane is in a fixed position. The reflection at such a fixed set of net-planes under a constant glancing angle  $\phi$  has therefore the effect of separating only a special wave-length  $\lambda$  out of the total number of wave-lengths present in the incident rays; it changes the incident radiation, being a complicated wave-motion, into a "monochromatic" one of definite wave-length  $\lambda$  corresponding to a certain glancing angle  $\phi$ , and therefore such a reflection has a pronounced selective action. It may be remarked here that  $V_1$  need *not* be a limiting plane of the crystal; the so-called reflection occurs *within* the crystal, and at the parallel, equidistant net-planes present therein.

When the radiation falling on the crystal is monochromatic, the

effect is still more restricted. For only at a few characteristic glancing angles  $\phi_1, \phi_2, \phi_3$ , etc., can reflections take place, these all being determined by the equation:  $2d\sin\phi = n\lambda$ .

The crystal in this case must be held at exactly the characteristic angle, and even then it can only give a spectrum of *one* order at the same time; in this respect it differs principally from an ordinary line-grating which may give at any angle of incidence spectra of different orders simultaneously. It follows from this that in the patterns previously considered, where the crystal-plate remained in a *fixed* position during the experiment, each spot on the photographic plate corresponds to a single, definite wave-length. If we could distinguish the "colours" of a Röntgen-radiation with continuous spectrum, as we do in *visible* light, we should see that the pattern would be a multi-coloured one, every spot having its own colour, wholly depending on the direction of the set of net-planes in the crystal from which the ray which produced that spot, took its origin.

§ 23. For our purpose the facts referred to in the preceding paragraphs may be considered sufficient. Indeed, if Röntgen-radiation of known wave-length  $\lambda$  be used, observation of the angles of reflection on a definite set of net-planes will give us a relation between  $\lambda$  and  $d$ , and by doing this for various known directions of a crystal, for instance for the three pinacoides  $\{100\}$ ,  $\{010\}$ , and  $\{001\}$ , etc., we shall gain an important insight into the dimensions  $d_1, d_2, d_3$ , etc., related to them.

The equation deduced in the above includes all we have to know for the study of the special arrangement of the net-planes in such a crystalline medium with respect to each other, and it was in this way, that W. H. and W. L. Bragg made their successful investigations of the internal structure of a number of crystals. Without considering their special methods of experimenting<sup>1)</sup> in detail, we shall only discuss here some of their results, in so far as they

<sup>1)</sup> The directions in which, on turning the crystal about an axis, real interference-maxima occur, can be found by several methods. The English investigators mentioned used for this purpose the ionising effect Röntgen-rays have on gas-molecules. The "indicator" of their X-ray-spectrometer was an *ionisation-chamber*, filled with a suitable gas, as for instance *sulphur-dioxide*. However it is equally possible to make use of other effects produced by Röntgen-rays, when these effects can be measured or observed even if they be very feeble. Many investigators have in recent times made use of the *photographic plate* (De Broglie, Friman and Siegbahn, Debije, and others), especially for the study of wave-lengths.

are important for testing our general conclusions as to the structure of the regular, unlimited, molecular systems to which we were led hitherto in this chapter.

§ 24. Every metal used in the *X*-ray-bulb as anticathode is stimulated to the emission of *X*-rays characteristic for that metal<sup>1)</sup>. Some of them give spectra of very few lines, most of them such of a somewhat more complicated structure, although the most intensive lines are also in this case rather small in number, and belong to only two different series which are commonly distinguished as *K*- and *L*-series.

Within a certain range of the spectrum, two or three of the most intense lines may be used for the experiments to be described further on, so that these are carried out with a source of radiation which although not monochromatic in the true sense of the word, gives results which ordinarily are easily controlled and interpreted.

Such rather simple *X*-ray-spectra can be obtained by means of anticathodes made from *palladium*, *rhodium*, *tungsten*, or *platinum*. The *rhodium*-anticathode chiefly emits rays with the wave-lengths:  $0,537.10^{-8}$  c.M.;  $0,545.10^{-8}$  c.M.;  $0,614.10^{-8}$  c.M. and  $0,619.10^{-8}$  c.M., — the latter being much more intense than the former. The *palladium*-anticathode gives radiations of  $0,583.10^{-8}$  and  $0,589.10^{-8}$  c.M., and of  $0,516.10^{-8}$  and  $0,503.10^{-8}$  c.M., while in another series there is again a wave-length of  $4,622.10^{-8}$  c.M. *Tungsten* emits a radiation of  $1,486.10^{-8}$  c.M., while a *platinum*-anticathode gives a spectrum with five principal lines, the wave-lengths of the most intense being:  $1,316.10^{-8}$  c.M. (*A*), a doublet of  $1,113.10^{-8}$  and  $1,095.10^{-8}$  c.M. (*B*), and a line of  $0,96.10^{-8}$  c.M. (*C*).

Let us suppose that an *X*-ray-bulb is used with such a *platinum* anticathode, of whose radiation we shall at present consider only the wave-lengths denoted by *A*, *B*, and *C*. A crystal of *sodium-chloride* may be so placed, that the "reflection" of the incident beam occurs at the cube-face (100) of the crystal.

Three maxima, of which *B* is the strongest and *C* the weakest, are found at glancing angles  $\phi$  of  $13^{\circ}48'$ ,  $11^{\circ}30'$  and  $10^{\circ}$  respectively.

They are repeated in a spectrum of the second order with somewhat smaller intensities, as  $A_2$ ,  $B_2$  and  $C_2$ , the corresponding glancing

<sup>1)</sup> W. H. and W. L. Bragg, *Proceed. Roy. Soc. London* **88**. A. 428. (1913); H. G. J. Moseley and C. G. Darwin, *Phil. Mag.* (6). **26**. 210 (1913); H. G. J. Moseley, *ibid.* (6). **26**. 1024. (1913); (6). **27**. 703. (1914).

angles being:  $27^{\circ}36'$ ,  $23^{\circ}30'$ , and  $20^{\circ}$  respectively; and finally as a spectrum of the third order with still smaller intensity, as  $B_3$  and  $C_3$ , at angles of  $35^{\circ}50'$  and  $30^{\circ}48'$ .

In agreement with the theory enunciated in the above, we find that:  
 $\sin 13^{\circ}48' : \sin 27^{\circ}36' = 0,238:0,463$ ;  $\sin 11^{\circ}30' : \sin 23^{\circ}30' : \sin 35^{\circ}50' = 0,199:0,399:0,585$ ; and  
 $\sin 10^{\circ} : \sin 20^{\circ} : \sin 30^{\circ}48' = 0,173:0,342:0,512$ ; — which ratios are very near to 1:2, or to 1:2:3.

If instead of *rock-salt*, the corresponding mineral *sylvine* ( $KCl$ ) be used, the phenomena observed when reflection occurs at the faces of the cube  $\{100\}$ , of the rhombicdodecahedron  $\{110\}$ , and of the octahedron  $\{111\}$  successively, are in two of the three cases wholly analogous in character, but for the same wave-length the glancing angles on each of the three faces are different, their sines being always in a constant ratio, exactly as in the case of *rock-salt*. Thus for instance corresponding maxima on (100), (110), and (111) are found here at  $5^{\circ}13'$ ,  $7^{\circ}18'$ , and  $9^{\circ}3'$  respectively, the sines of which are in proportion of  $1 : \sqrt{2} : \sqrt{3}$ .

The same ratio would be found for the sines of the angles, at which corresponding maxima occur on the faces (100), (110), and (111) in the case of *rock-salt*, although the *absolute* values of these angles are other than with *sylvine*.

It is obvious that this constant ratio is exactly the same as that of the *inverse distances* of the consecutive layers parallel to the three faces mentioned in a *simple cubic space-lattice*. For if we take the three possible types of arrangements in cubic space-lattices (p. 118), we have:

Type of Space-lattice:		Ratio: $\frac{I}{d_{(100)}} : \frac{I}{d_{(110)}} : \frac{I}{d_{(111)}}$
1.	<i>Simple Cubic Arrangement.</i>	$1 : \sqrt{2} : \sqrt{3}$
2.	<i>Cube-centred Arrangement.</i>	$1 : \frac{1}{2}\sqrt{2} : \sqrt{3}$
3.	<i>Face-centred Arrangement.</i>	$1 : \sqrt{2} : \frac{1}{2}\sqrt{3}$

§ 25. The behaviour of the *sylvine*-crystal towards the Röntgen-radiation can therefore easily be explained when the supposition is made that the radiation observed is produced by particles arranged

in a simple cubic space-lattice. Now experience shows that the intensity of the secondary radiation produced by Röntgen-pulses passing over atoms, is intimately connected with their atomic weight; more particularly it appears *that the amplitude of the waves reflected by each net-plane is nearly proportional to the total mass of the atoms lying in that net-plane*. If the number of particles in two successive net-planes is the same, the ratio of the amplitudes of the waves reflected by them, will be therefore almost the same as that of the individual masses of both net-planes. And because the atomic weights of *potassium* ( $= 39$ ) and of *chlorine* ( $35,5$ ) are only slightly different, it will be understood that these atoms will behave nearly as if the particles arranged in the cubic space-lattice were really *all of the same kind*.

But when *sodium-chloride* is used in the experiment, experience shows that the character of the reflection at the faces of (100) and (110) is exactly analogous to that observed at

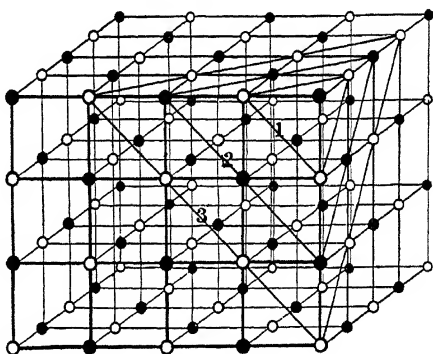


Fig. 124.

Structure of *Potassium*-, and *Sodium-chloride*.

the same faces of the *potassium-salt*. The reflection at (111) however, manifests an additional phenomenon in comparison with the corresponding reflection in the case of *rock-salt*, in so far as the maximum intensity now corresponds not only to a glancing angle of  $21^\circ$ , as would be expected with regard to the reflection at the *potassium-chloride*-crystal, but *moreover* to another angle of about  $10^\circ 30'$ . The maximum is here somewhat feebler than the first mentioned one.

The cause of this difference is explained by the fact that the atomic weight, and therefore the power of emission of *sodium*- and *chlorine*-atoms, differ much more than those of *potassium*- and *chlorine*-atoms. Indeed, if in the simple cubic space-lattice of *fig. 124*, in which the black dots are the metal-atoms and the white ones the halogen atoms, we make sections parallel to (100) or (110), these consecutive sections will all prove to be *identical*, consisting of equal

numbers of metal- and halogen-atoms. But if we make sections in a direction perpendicular to a trigonal axis of the space-lattice, we have layers of metal-atoms alone, alternating with layers consisting only of halogen-atoms. In the case of *potassium-chloride*, where *K* and *Cl* with respect to their secondary emission behave almost identically, the result of the interference of the reflected rays is nearly the same as when all layers are built up by same the kind of particles. In the case of *sodium-chloride*, however, this is no longer the case; here the result of the interference of rays coming from the layers 1, 3, 5; 7, etc., will be different from that of the waves coming from the alternating layers 2, 4, 6, 8, etc. The latter will of course have a phase *opposite* to that of the first series; but as their *amplitudes* are *different*, they will not completely counterbalance each other, and a second maximum, as mentioned above, is therefore observed here <sup>1)</sup>.

The structure of both salts is therefore much the same: both systems consist of two interpenetrating cubic face-centred space-lattices, the one of which is built up by *chlorine*-, the other by *metal*-atoms, and so intercalated that the *chlorine*-space-lattice is shifted over a distance of half the cubic-edge of the *metal*-space-lattice,

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1) When  $a$  and  $a'$  are the amplitudes of the waves reflected by the planes 1, 3, 5, 7, etc. consisting of *metal*-atoms, and 2, 4, 6, 8, etc. consisting of *chlorine*-atoms respectively, and when  $\varepsilon$  is the phase-difference produced by the reflection at two consecutive layers of the whole parallel set, the *resulting* amplitude  $A$  produced by the interference, may be represented by an equation of the form:

$$A = a \cos(nt) + a' \cos(nt - \varepsilon) + a \cos(nt - 2\varepsilon) + a' \cos(nt - 3\varepsilon) + \dots \text{etc.}$$

If  $a$  were equal to  $a'$ , we should have a maximum for  $\varepsilon = 2\pi, 4\pi$  etc., but for  $\varepsilon = \pi$ , the value of  $A$  would become *zero*, because every two consecutive terms of the sum would counterbalance each other, their phases being exactly *opposite*. When  $a$  and  $a'$  are however *not* equal, there will besides the maxima mentioned in the preceding case, also be some feebler ones for  $\varepsilon = \pi$ , because these oppositely directed vibrations now *no* longer counterbalance each other, their intensities being *different*. This is the analytical expression for what is said here. If the consecutive layers of different atoms did not follow each other in equal distances, but e. g. in such a way that every layer of the one kind of atoms divided the distances  $d$  of two consecutive identical layers of the other kind in a ratio of 1 : 3, we should have:

$$A = a \cos(nt) + a' \cos(nt - \varepsilon) + a \cos(nt - \frac{1}{4}\varepsilon) + a' \cos(nt - \frac{5}{4}\varepsilon) + a \cos(nt - 2\varepsilon) + \dots \text{etc.}$$

Now there will be a maximum for  $\varepsilon = 2\pi$ , and a feebler one for  $\varepsilon = 4\pi$ . The two first vibrations of the series will be:  $a \cos(nt)$  and  $a' \cos(nt - \pi)$ ; they are oppositely directed, but do *not* nullify each other, because  $a$  and  $a'$  are *different*. This is the case observed in *zinc-sulphide*.

each *chlorine*-atom thus falling midway between two consecutive *metal*-atoms, and vice versa.

The different behaviour with respect to the reflection at (111) is fully explained by the difference of atomic weights in the case of *K* and *Cl*, and of *Na* and *Cl*.

However there is again further evidence as to the correctness of these conclusions. In comparing the behaviour of both crystals with respect to the reflection at *the same* face, let us say at (100) or (110), — it is obvious that they are *similar*, but, as it were, executed "on a different scale". This scale is governed by a constant proportion in so far, as the sines of the corresponding glancing angles on the same faces of *KCl* and *NaCl* prove to be nearly = 1,12. The explanation of this fact is very simple indeed: it is caused by the difference in magnitude of the distances *d* between corresponding consecutive layers in both crystals. If therefore it be observed that the ratio  $\frac{\sin \Phi_{(NaCl)}}{\sin \Phi}$  is about = 1,13, we can conclude that

this is the same for  $\frac{1}{d_{(NaCl)}} : \frac{1}{d_{(KCl)}}$ ; and it is easily calculated from the molecular weights  $M_1$  and  $M_2$  (74,6 and 58,5) of both salts and from their densities  $s_1$  and  $s_2$  (1,99 and 2,17), that this ratio is almost exactly the same as that of the *edges* of two cubes, each of which contains one mol of the salts; these edges are 3,35, and 3,00 c.M. respectively. The number of molecules present in such a cube is however known. For the absolute weight of a *hydrogen*-atom is  $1,64 \times 10^{-24}$  gram, that of a mol *sodium-chloride* therefore  $95,94 \times 10^{-24}$  gram. The number of molecules *NaCl* in the cube with its edge of 3,00 c.M. is therefore  $\frac{58,5}{95,94 \times 10^{-24}} = 0,610 \times 10^{24}$ , or  $1,22 \times 10^{24}$  atoms. On every edge of the cube there are as a consequence:  $1,07 \times 10^8$  atoms, their mutual distance therefore being  $\frac{3,00}{1,07 \times 10^8}$  c.M. =  $2,8 \times 10^{-8}$  c.M.

The spacing of the layers parallel to (110) or (111) is then easily calculated from this number, while that of the consecutive layers of *KCl* parallel to (100), is of course  $3,15 \times 10^{-8}$  c.M. etc.

§ 26. The cases of *sodium*-, and *potassium-chloride*, discussed more in detail, may give an idea of the general method of reasoning followed by Bragg to try to find out the internal structure of crystalline substances. The study of the relative intensities of the spectra of the first, second, third order, etc., and of other peculiarities of



them, as for instance in the case of *diamond*, where the second spectrum was completely cut out, — requires a number of conditions to be fulfilled, before the arrangement adopted really explains the diffraction-phenomena observed in every special case.<sup>1)</sup>

More particularly the *face-centred* space-lattice of cubic symmetry, so closely related to the *most closely packed* arrangement, appears to be of high importance for the internal structure of cubic crystals. Thus in the case of *zinc-sulphide*, the *zinc*-atoms are arranged in such a face-centred cubic lattice, while the *sulphur*-atoms are disposed through the system in such a way that they occupy the centres of half the number of the eight smaller cubes in which the greater face-centred cubes of the *zinc*-atoms may be imagined to be subdivided; in this case two of these smaller cubes must never be adjacent to each other.

When the *zinc*- and the *sulphur*-atoms in *ZnS* are all substituted by *carbon*-atoms, the structure of *diamond* is obtained, such as it must be with respect to the experimental results met with in the study of its crystals. That there, contrarily to what was observed in the case of *ZnS*, the spectre of the second order ( $\epsilon = 2 \times 2\pi$ ) is completely cut out in the reflection at the octahedron-faces, is explained by the fact that the alternating layers all consist of *identical* atoms, the amplitudes  $a$  and  $a'$  of both oppositely directed secondary vibrations being therefore *equal* in this case. The waves reflected under this difference of phase will therefore *totally* destroy each other, which was not the case when they were emitted by alternating layers of *zinc*- and *sulphur*-atoms.

With respect to the structure of *diamond* it may be remarked that the whole arrangement is such that each *carbon*-atom is surrounded by *four* others, placed in the corners of a *regular tetrahedron*, the centre of which is occupied by the first named *carbon*-atom. This arrangement is in striking agreement with the suppositions once made by Van 't Hoff and Le Bel with respect to the direction in space of the four valencies of the *carbon*-atom in general.

Recently Debije<sup>2)</sup>, by means of his most ingenious method of observation, studied the structure of *graphite*, and of other allotropic

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<sup>1)</sup> The question may be raised: can the supposed structures be the *only* true ones, excluding every other possible arrangement? According to Barlow (Proc. Roy. Soc. London, **91**. 1. (1915), the possibility of other explanations as given by Bragg, seems to be undeniable.

<sup>2)</sup> Private communication to the author. The paper considered will be published within a short time.

forms of *carbon*, which all appear to have the same structure as *graphite* itself. He found that the *carbon*-atoms are placed here in the corners of regular hexagons arranged in parallel strata, the fourth valency of the *carbon*-atom being reduced to an extremely weak force. This fact seems to prove that the *carbon*-atom can act as a centre either of *four*, or of *three* equal valencies, and the phenomena observed give to some extent an explanation of the possible occurrence of derivatives of *trivalent carbon* (as *triphenylmethyl*, etc.) and of the specific nature of the "aromatic" nucleus with its "paralysed" valencies.

§ 27. Without going into further details of these highly important investigations, or into the discussions and problems which they entail, we may bring to the fore the following salient points from the above:

a). Direct experimental proof is given of the correctness of the view that the component particles in crystals are arranged in space-lattices, as was already foreshadowed by crystallographers some sixty years ago.

b). Direct proof is given of the correctness of the other view (Sohncke, Groth<sup>1)</sup> that the unlimited regular structures we call *crystalline substances*, may be considered as being built up by the regular interpenetration of such space-lattices, each of which consists of one and the same kind of atoms. These atoms plainly preserve therefore their individuality as constituents of such crystalline substances.

c). Because of the periodical character of these unlimited regular systems, it is from a mathematical and crystallographical point of view absolutely arbitrary, in which way we wish to imagine these atoms to be combined into larger units, although we have at present no idea, in what way and by what forces the "chemical molecule" is preserved in such a structure<sup>2)</sup>.

The notion of "crystal-molecule" as a structural unit has therefore lost its significance from a *crystallographical* standpoint: the whole crystal, endlessly extended in all directions, is one single gigantic

1) P. Groth, Ber. d. d. Chem. Ges. **47**. 2063. (1914); Zeits. f. Kryst. **54**. (1915). According to this author the interatomic connections must remain, even if from a crystallographical point of view the chemical molecule as such has lost its significance. Many crystals have symmetry-elements, the special nature of which is obviously closely related to the atomic structure of the chemical molecule itself. This can only have any significance, if the latter remains present in the crystal.

2) Most recently J. Beckenkamp (Centralbl. f. Miner. (1917), p. 97—110 has made some suggestive suppositions about the preservation of "chemical molecules" in crystalline media.

crystal-molecule. There is, however, at present no reason why the existence of special forces preserving the atomic relations previously existing in the separate chemical molecule should be denied, as has been done in recent times by a number of scientists <sup>1)</sup>.

§ 28. One of the most important problems of the immediate future must be to get information about the special connection between the forces which hold together the regular arrangements in space of the atoms composing the crystalline medium, and the chemical forces or valencies supposed to be the causes of the chemical architecture of the molecule itself. Certainly there must be an intimate relation between them, as was for instance seen in the case of *diamond* and *graphite*, although we do not know at present how to attack this problem properly. The modern views on *coordination*, as proposed by Werner, seem to open a road in this direction: the forces which govern the structure of coordinative compounds appear to differ, not principally at least, from those supposed by the elder atomists.

When we shall have gone so far as to have found out this relation, the significance of the symmetry-principle for the mode of action of the chemical forces and for the stereometrical configuration of the chemical molecule itself, will then doubtless be seen in a new light, thus extending the views expounded in the previous chapters to the ultimate particles of inanimate matter also.

§ 29. In the preceding chapters we have also had full opportunity to draw the attention of the reader to the part which the principle of symmetry plays in living nature. The questions relating to this have two sides: either we can study the special *symmetry of the different organs* of living individuals; or we can regard more particularly the symmetry of *the mutual arrangement of such organs*. Hitherto we have dealt more exclusively with the first side of the question, which to some extent can be formulated in a way comparable with the second problem, by defining it as the question about *the arrangement of the different parts within these limited organs themselves*.

But as a plant or an animal increases its volume continuously by growth, and only secondary influences like the exhaust of life-energy, sexual functions, etc., will help to put a limit to this growth within a finite time, although without these hindering causes it properly would go on infinitely, — the living organism can also be looked upon as being *endless*, and an *unlimited* system like those

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<sup>1)</sup> Cf. the note on p. 153.

we have discussed in the above. Exactly as the growth of a crystalline medium is only bounded\* by secondary circumstances existing in its mother-liquid or its immediate environment, while from a theoretical point of view, it is also an endlessly extended system of regularly arranged units.

In this connection some considerations may be inserted here concerning the remarkable views about *phyllotaxis*, i. e. about the way of arrangement of leaves in plants. As we shall see, these phenomena are in many points very analogous to those dealt with in the preceding paragraphs. Closely related to them are the peculiarities observed in the arrangement of buds, of scales, and of the different parts of muscles etc., as observed in oceanic conchifers.

The fact that the leaves of plants are arranged in spiral series about their axis, has long been observed and recognised by botanists. The spiral-theory of *phyllotaxis* has since the days of Goethe and Bonnet<sup>1)</sup> often been a subject of investigation and speculation, and for a considerable time it has been an object of botanical interest, since its development by Schimper and Braun<sup>2)</sup> and by A. and L. Bravais<sup>3)</sup>.

Its fundamental conception is that the arrangement of such leaves occurs in series which form alternating rows when viewed in a horizontal or vertical direction. Thus proceeding along such a spiral line, we shall meet a definite number of leaves ("members" of the series), until after one or more revolutions a leaf is reached, which stands exactly vertically above the first one. The members included in such a series form together a *cycle*; the row of vertically superposed leaves are called *orthostichies*, while the parallel spirals are named *parastichies*. The cycle is indicated by a numeral symbol in the form of a *fraction*, like:  $\frac{1}{2}$ ,  $\frac{1}{3}$ ,  $\frac{5}{13}$ , etc., the numerator of which indicates the number of turns of the spiral in each cycle, while its denominator indicates the number of members inserted in each cycle. As an instance of this, we have in *fig. 125* reproduced the plane projection of such a spiral arrangement on a conical surface, in which *five* members are included in a cycle of *two* revolutions ( $\frac{2}{5}$ ). The *orthostichies* (e. g., 2-7-12) are projected as the radii of the system of circles, while

1) Ch. Bonnet, *Recherches sur l'Usage des Feuilles dans les Plantes*, Goettinge et Leyde, (1754). p. 159.

2) K. F. Schimper and A. Braun, *Flora*, 2. (1835); A. Braun, *Nova Acta Acad. Carol. Leopold. Nat. Curios.*, Halle, 15. 1. p. 195. (1831).

3) A. and L. Bravais, *Ann. des Sciences naturelles* (2) 7. p. 42, 67. (1837).

for some members a right, and a lefthanded wound parastichy

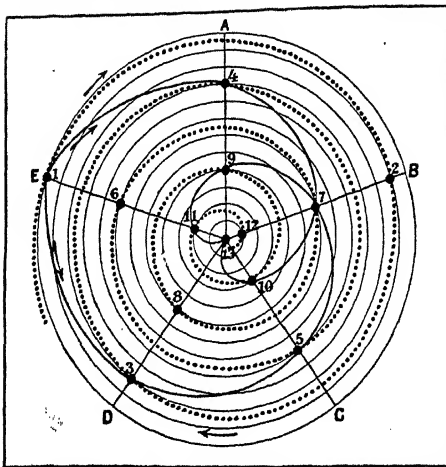


Fig. 125.

Plane projection of a spiral arrangement ( $\frac{2}{5}$ ) on a cone.  
 .... Genetic spiral.      ——— Parastichies.

has been drawn, to the significance of which we will draw attention afterwards.

Bravais determined Braun's "divergence" of two consecutive leaves by *angular* measurements, expressed in degrees of arc, the magnitude of this angle being of course directly related to the fractional symbols mentioned in the above. As beautiful examples

of such spiral arrangements may be mentioned: the ripened carpellary cones of *Pinus*, the fruit-bearing capitulum of the ordinary sunflower (fig. 126) (Church), the multiple fruit of *Ananassa* (fig. 127) with its consolidated mass of berries, and with their bracts round the axis, and finally the phyllotaxis of *Euphorbia Wulfeni*, according to Church. The number can be easily augmented.

Such a periodical arrangement evidently possesses the characteristics of a *space-lattice* wound upon a cylindrical surface. There are thus definite *translations*, by which the fundamental space-lattice is determined as by a special kind of symmetrical operations. If rolled round the cylindrical surface, the divergence of consecutive

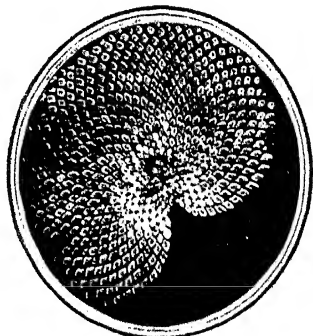


Fig. 126.

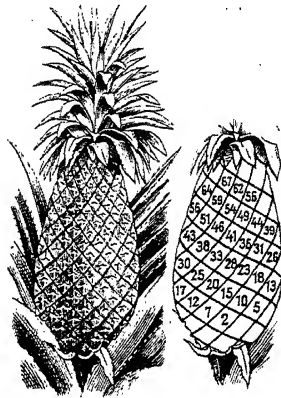
Fruits in the capitulum of the sunflower.

leaves on the *genetic spiral* (dotted line) may be expressed by a fraction, the values of which as found in nature<sup>1)</sup>, belong, among others, to the remarkable series:  $\frac{1}{2}$ ,  $\frac{1}{3}$ ,  $\frac{2}{5}$ ,  $\frac{3}{8}$ ,  $\frac{5}{13}$ ,  $\frac{8}{21}$ ,  $\frac{13}{34}$ , etc. Each fraction therein is obtained from both the preceding by addition of their numerators and denominators respectively. The series of these numbers was already studied by Leonardo Pisano (Fibonacci; 1180 — 1225), by Kepler, Lamé, Bravais, and other mathematicians. More especially it may be remembered that these fractions represent the successive values of the stages of the continuous fraction:

$$\frac{1}{2 + \frac{1}{1 + \frac{1}{1 + \frac{1}{1 + \text{etc.}}}}}$$

values which oscillate alterna-

tely towards the positive or negative with respect to a definite *limiting number*, to which the successive terms continuously approach more closely. This true *limit*-value is no other than the *irrational* number  $\frac{1}{2}(3 - \sqrt{5})$ , which represents the smaller portion of the ratio known as the "aurea sectio", — a ratio which since the days of Leonardo da Vinci (1452—1519) has been considered to be



intimately connected with all questions about ideal visual beauty of proportion in art and natural forms<sup>1)</sup>.

The "ideal" arrangement in phyllotaxis, towards a "tendency" in living nature appears to exist, should therefore be considered such that a spiral arrangement is attended to, whose characteristic angular divergence is equal to  $\pi (3 - \sqrt{5})$ , i. e. to  $137^\circ 30'28''$ . In this case true "orthostichies" do no longer exist, because there can *never* be a leaf standing *exactly* above some other, except in infinity. In the opinion of the adherents of this theory, the "ideal" disposition of leaves about a cylindrical stem aimed at by nature, would therefore be such as to prevent each leaf from overlapping another, even if the plants were so closely packed together as is often the case in dark tropical forests. The question, in how far this teleological view must be considered as being a mere fiction, or in real agreement with the natural adaption of the plant to its need of light and free air, may be passed over here<sup>2)</sup>.

**§ 30.** If the theory of phyllotaxis just explained be once adopted, and if the forms of the parastichies on a cylindrical stem be supposed to agree with that of the ordinary Archimedian spirals ( $p = a.s.$ ), the development of the system of parastichies on the cylindrical surface in a plane will give a system of parallelogram-shaped meshes, at the corners of which are placed the different leaves. Such a plane drawing, showing the arrangement of the bracts and berries observed in a part of the multiple fruit of *Ananassa sativa*, is reproduced in *fig. 128*.

As Wulff<sup>3)</sup> first pointed out, the distribution of these organs is, at least in principle, exactly comparable with the space-lattice-structure met with in crystalline matter, this form of structure

<sup>1)</sup> Let a straight line  $AB$  be equal to unity, and  $C$  be a point so situated on it, that  $AC : CB = AB : AC$ . Then  $AC^2 = AB \cdot BC$ , from which follows that  $BC = \frac{1}{2} (3 - \sqrt{5})$ , and  $AC = \frac{1}{2} (\sqrt{5} - 1)$ . This division of  $AB$  by the point  $C$  is called the "golden section", or "aurea sectio" (also: *sectio divina* or *divina proportio* (Kepler)), the length of both portions is 0,381988... and 0,618034... respectively. The relations of this ratio to the properties of the regular pentagon, and therefore to *pentagonal symmetry* in general, are well-known.

<sup>2)</sup> J. Wiesner, *Flora* (1875), p. 115, 139, 142; *Biol. Centralblatt*. 23. 209, 249, (1913); H. Winckler, *Pringsheim's Jahrbuch f. wiss. Botan.* 36. 1. (1901). Wiesner concludes: "Regular phyllotaxis as determined in the sense described above, is a phenomenon doubtless intimate lyconnected with the question of the most suitable adaptation to the natural conditions of light-absorption by plants".

<sup>3)</sup> G. W. Wulff, *Symmetry and Its Manifestations in Nature*, (Russian), Moscou (1907), p. 119. etc.

being indeed the prototype of the most general periodical distribution of equal things in unlimited number. But yet there must appear to be a striking difference between the arrangement of living objects in one case, and that of the molecules in the other. For if all conditions in phyllotaxis were really such as pictured here, the divergencies which occur would be such that their numerical symbols could be only *rational* numbers, — just in the same way as the possible edges of a crystal are always determined by the direction of some straight line joining the angular points of each net-plane.

However, as we have seen, it is found by experience that only symbols closely related to those of the series mentioned above occur

in living nature, and that there is thus rather a tendency towards the *irrational* ratio of the "aurea sectio" in living nature, — which to some extent goes parallel to the preference for true *pentagonal* symmetry stated in the preceding chapters of this book.

Wulff tries to show that this contrast is only an *apparent* one, pointing to the fact that even in such a crystallographically admissible space-lattice, irrational "limit"-values might be indicated.<sup>1)</sup> If a straight line for instance joins the angular point of such a net-plane, which has the coordinates  $(8, 21)$ , with the origin  $O (= 0, 0)$ , it passes alternately *above* and *beneath* the angular points  $(5, 13)$ ,  $(3, 8)$ ,  $(2, 5)$ , etc., of the net-plane, and it approaches the closer

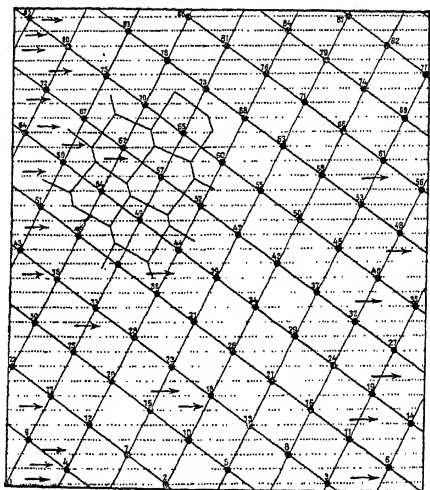


Fig. 128.

Genetic spiral (laevogyrate).

— Parastichies  $(8 + 13)$ .

<sup>1)</sup> G. W. Wulff, loco cit.



towards these points, the farther the original point ( $m, n$ ) was chosen distant from  $O$ , that original point being determined, for instance, by coordinates like  $m = 34, n = 89$ , etc. The angular points mentioned have the coordinate-fractions characteristic for the consecutive terms of the Fibonacci series; and the straight line considered will, in infinity, pass through the point, having the irrational coordinates:  $N[(3-\sqrt{5}), 2]$ . However it is clear, that there is in the whole net-plane infinitely extended, *no* such point really present; and it cannot be maintained that a parallelism between the space-lattice character of crystals, with their rational ratios, and living organisms is really established by this way of reasoning, suggestive as for the remaining it may be. For the generatrix of the cylindrical stem would in this case be a line of the supposed space-lattice, which does *not* pass through any real angular point of the net-plane considered; this straight line would therefore in a crystalline medium have *no* significance at all. Instead of supporting such a parallelism between the two groups of phenomena, the fundamental contrast between living and inanimate nature with respect to form-symmetry, is again more strikingly brought to the fore by these considerations, in so far as what is impossible in the one domain of phenomena, should even be the most perfect state of things in the other.

§ 31. However it must be borne in mind that we have no right to consider these remarkable views on phyllotaxis, as pictured in the above, to be of real *ontogenetic* significance, as long as we have no indications about the mechanical or physiological causes of such mathematically determinable arrangements of similar organs.

In this respect now it is of importance to remark that the correctness of the theory of phyllotaxis mentioned, as developed by Bravais, Schimper and Braun, has been partially contested in later times by several workers in this field of research, for instance by Hofmeister<sup>1)</sup>, Sachs<sup>2)</sup>, Church<sup>3)</sup> and others.

The latter has demonstrated in a convincing way that the determination of a member exactly vertically superposed to one taken as a point of reference, is practically impossible, either by direct observation, or by angular measurements as proposed by Bravais. Direct observation teaches that a leaf perhaps *never* stands vertically above any

<sup>1)</sup> W. Hofmeister, *Allgemeine Morphologie der Gewächse*, (1868).

<sup>2)</sup> J. Sachs, *Vorlesungen über Pflanzenphysiologie*, Leipzig, (1882). p. 603, 606; S. Schwendener, *Mechanische Theorie der Blattstellungen*, (1878).

<sup>3)</sup> A. H. Church, *On the Relation of Phyllotaxis to Mechanical Laws*, (1904).

given one, a fact already stated in some exceptional cases by Bravais. All so-called "orthostichies" seem to be really *curviserial* lines, especially in the higher divergencies. But then they cannot be distinguished principally from parastichies, and therewith one of the premises of the Schimper-Braun-theory has lost its value.

Church concludes that *only the number of intersecting parastichies, dextro-, or laevogyrate, determines the numerical character of the arrangement*, as already suggested by Braun. Moreover he points to the fact already stated by Hofmeister, De Candolle and Sachs, that the phyllotaxis-fraction, whatever numerical value is given to it, must *appear* greater or smaller in the same rate, as the axis about which the leaves are arranged, is shortened or lengthened, the phenomena of *varying* phyllotaxis therefore being partially caused by the *varying rates of growth*<sup>1)</sup>. De Candolle<sup>1)</sup> has drawn attention to the same fact; according to this author the character of the phyllotaxis, — even if a constant angular divergence between consecutive members be supposed, — must vary when the ratio:  $\frac{\text{length}}{\text{diameter}}$  of the stem during the process of growth changes appreciably. In condensed and multiple fruits and inflorescences (*Pinus*, *Ananassa*, *Helianthus*, etc.) a change of the ratio between longitudinal and transversal growth does *not* occur; hence the laws of phyllotaxis are best studied in the case of such multiple fruits and inflorescences, in the capitulum of the sunflower, in the cones of *Pinus*, in terminal buds, etc. It is therefore absolutely necessary to draw attention more exclusively to the study of the *growing apex of the plant*: the *first* zone of growth in the terminal bud must, in the opinion of this author, reveal the phenomena of phyllotaxis in their most pure and undisturbed form. The explanation to be given of it must moreover really satisfy the requirements of ontogenetic observation. Thus, starting from Sachs' theory of cell-formation and of the *orthogonal* intersection of cell-walls<sup>2)</sup> in the terminal bud, he comes to the conclusion that the parastichies must have the shape of *logarithmic*

1) Cf.: G. v. Iterson Jr., *Mathematische und Mikroskopisch-anatomische Studien über Blattstellungen*, Jena, (1907), p. 222. C. de Candolle, *Considérations sur l'Etude de la Phyllotaxie*, Genève, (1881), p. 47, 29, 52. There seem to be however a number of other important causes, acting during the first design of the lateral organs, which govern this phenomenon of varying phyllotaxis.

2) J. Sachs, *loco cit.* p. 253; Cf. also: L. Errera, *Bull. de la Soc. belge de Microscopie*, 18. 1. (1886).

*spirals* ( $\rho = a^z$ ), intersecting everywhere at right angles. Indeed, in two-dimensional space the logarithmic spiral is the only curve, in which one part differs from the other only in *size*, but *not in shape*, — a property which brings out very strikingly the essential character of such curves as *lines of growth*.

If it be kept in mind that the primordial cells will be greater as

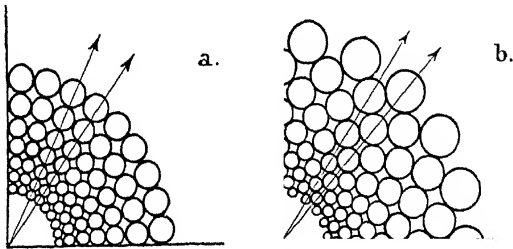


Fig. 129a and b.

they are older, Church gives the following constructions of the spiral arrangements in the first *zône* of growth. As symbols of the emergences based on lateral members of cell-aggregates, he takes, like

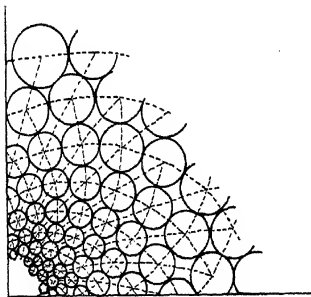


Fig 130.

De Candolle (loco cit. p. 52), circles of different diameter packed closely together in the way of the most closely packed "cubic" arrangements (fig. 129a and b, and in both principal directions (cf. fig. 121), as well *laterally* (fig. 129a) as *diagonally* (fig. 129b) oriented along the radii of all-sided growth. The "diagonal" arrangement corresponds to the special supposition that a new member

takes its place precisely in the cavity left between two members already present. The radial arrangement is in agreement with the radial direction of transversal growth (De Candolle, loco cit. p. 29). Now the concentric circles indicating the successive *zônes*, are substituted by a logarithmic spiral as "genetic" line, "like the line of current in a spiral vortex", and the radii likewise substituted by parastichies of the same shape wound in one or in the opposite direction.

Thus, in the case of "diagonal" orientation the asymmetrical system of *fig. 130* appears; and how closely these constructions, — which can moreover be performed in a simple geometrical way, — lead to arrangements corresponding with what is observed really in nature, — may be seen by comparison of Church's *fig. 131*, which represents the configuration of fruits in the capitulum of *Helianthus annuus*, as deduced from his theory, with the arrangement of the fruits really observed, as represented in *fig. 126*. In this construction the whole system remains *orthogonal*, as was originally planned with regard to Sachs' theory mentioned above<sup>1)</sup>.

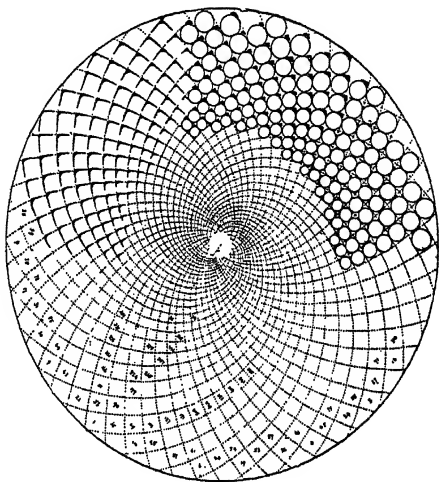


Fig. 131.

Church's construction of the Configuration of the fruits in the Capitulum of *Helianthus annuus*.

§ 32. As to the *numerical* relations expressed by this theory, in which the *orthostichies* have wholly lost their significance, the following remarks may be made here.

The system of intersecting parastichies is indicated by two numbers, as for instance  $(34 + 55)$  in the case of *Helianthus* for the inplantation of the individuals in its capitulum-disk, or  $(8 + 13)$  for that of the bracts in the multiple fruit of *Ananassa* (*fig. 127*). Of these numbers the first refers to the longer, the second to the shorter spiral (see *fig. 125*). The symbols mentioned above, would be  $\frac{34}{88}$  or  $\frac{8}{31}$  in the Schimper-Braun-theory; and in an analogous way as therein the series of fractions indicated previously is arrived at, we can write the "normal" series in the new symbols as follows:

<sup>1)</sup> Recently some doubt has arisen also about the correctness of Sachs' original view, concerning the "orthogonal" intersection of newly formed cell-walls. J. C. Schoute; private communication to the author.

(1 + 1), (1 + 2), (2 + 3), (3 + 5), (5 + 8), etc. Here also the successive values approach gradually to a limit:  $1 - \frac{1}{1,618} = \frac{3-\sqrt{5}}{2}$ , and the ratios naturally adopted by the plant for its intersecting parastichies are the successive terms of the continuous fraction:

$$\frac{1}{z + \frac{1}{1 + \frac{1}{1 + \frac{1}{1 + \text{etc.}}}}}$$

In a great number of cases  $z$  is equal to unity in this fraction. These values would for growing plants with a definite number of leaves give the optimum approach to a symmetrical distribution in such a spiral system. However it may appear doubtful whether the mechanical or physiological causes of this leaf-distribution are really better explained by this mode of reasoning than by previous views<sup>1)</sup>.

The true "pentamery" as observed in the flowers of many *Dicotyledons* and in many *lower animals* (Chapter III and IV), is a special case of this ideal arrangement, and in truth the most highly perfected condition of phyllotaxis<sup>1)</sup>, expressed by the special symbol (5 + 5).

In this respect a certain tendency of living nature to the ratio expressed by the "aurea sectio" may be stated again, — a fact already pointed to in 1611 by Kepler in some of his botanical speculations.

But it must be clear from the above that in the light of this theory all supposed analogy with the arrangement of the molecules in crystals, as suggested by Wulff, vanishes completely now. Church expressly points out that *no* Archimedian spirals ever play a rôle in natural phyllotaxis<sup>2)</sup>, and therefore the development of such a spiral in a plane does *not* give a system of points endowed with the peculiarities of a Bravais' net-plane.

The result in this case will rather be a system of logarithmic curves, to which no reasonings as brought to the fore by Wulff, can be immediately applied. Only more complicated and elongated relations exist between these logarithmic spirals<sup>3)</sup> and the helices

<sup>1)</sup> G. van Iterson Jr. loco cit., p. 106, 108, and 144. (1907).

<sup>2)</sup> Cf. G. van Iterson Jr., loco cit., p. 1. (1907).

<sup>3)</sup> A. H. Church, loco cit.

on a cylindrical or conical surface. There is no question about such *simple* connections between the internal structure of crystals and the phenomena of phyllotaxis, as suspected by the Russian scientist. The essential difference between the two cases remains this, that all kinds of net-planes can, with a greater or smaller probability of occurrence, have the function of crystal-facets, while of all theoretically possible regular distributions of the loci of leaf-attachment in plants only those are realised by nature, whose divergencies approach closely to those expressed by the fractions of the principal series indicated in the above, or of series deduced from it in a simple way.

## CHAPTER VII.

### MIMETIC FORMS AND APPARENT SYMMETRY.

Observed Disagreements between Crystallographical and Physical Symmetry. — Crystal-Aggregates in General. — Twinning: general Remarks. — Repeated Twinning: Cyclic and Polysynthetic Twins. — Forms of Approximate Symmetry. — Pseudo-Symmetry. — Mimetic Forms. Mimicry and Pseudo-Symmetry. — Compound Twinning of Microscopical Lamellae of Approximate Symmetry. — The Explanation of Optical Anomalies. — Examples. — Mallard's Theory of the Optical Behaviour of crossed Lamellae. — The Rotatory Power of Crystals. — Pseudo-symmetry and Polymorphism. — Mallard's Views about the Pseudo-symmetrical Character of all Crystalline Matter. — Final Remarks.

*„Cette tendance vers la Symétrie est une des grandes lois de la nature inorganique . . . Elle n'est d'ailleurs qu'une manifestation de la tendance plus générale de la Nature vers la stabilité, c'est-à-dire vers le repos, — tendance, qui est une des grandes forces antagonistes de l'Univers.”*

E. Mallard, 1880.

§ 1. In the previous chapters we have repeatedly had occasion to observe, how the symmetry-principle and its laws find application in all considerations regarding crystalline matter and its inherent properties. Indeed, with respect to their external appearance no less than with respect to their internal structure, crystals are objects whose behaviour is chiefly governed by the laws of symmetrical configuration. In general it may appear that no essential discordances exist between the external forms of each crystalline individual and its molecular structure; and the world of crystals appeared from this to be rigorously ruled by stubborn laws which do not allow any ex-

ception in the behaviour of the individuals which have a part in it.

However on closer examination, this appears to be by no means the case under *all* circumstances. In this well-governed society too, with its clear lines of demarcation and its strictly defined distinctions of classes and systems, there are a number of individuals which behave certainly not as they should do. Numbers of eccentricities are to be noted, and the somewhat revolutionary manifestations of many individuals take place here in a similar degree, as in our much more insufficiently ruled human society.

In the present chapter we propose to deal with some of the phenomena indicated, and as experience has taught that even these crystallographical eccentricities conform to certain well determined laws, let us see first, what remarks and attempts at an explanation of the peculiar behaviour of these eccentric individuals, have been made up till now.

§ 2. Since Romé de l'Isle and Hauy, it has been stated by several observers that many crystals have a strong tendency to form more or less complicated *aggregates*. This fact has been met with innumerable times especially among minerals, and of some of them this tendency seems to be so characteristic, that separate crystals of such minerals must be reckoned among the greatest mineralogical rarities.

Whether crystals will deposit from a solution as separate individuals, or as a confused aggregation of irregularly situated crystals, seems to be determined by special circumstances of deposition-*velocity*, and by the fact that crystallisation may take place *quietly* or *not*. Indeed, if the solution be strongly agitated or irregularly moved during the process of crystallisation, an aggregate of small crystals directed towards all sides is commonly the result. Such crystal-aggregates may be completely irregular: a heap or a crop of arbitrarily grown needles or plates will be present, and no definite relation whatever will exist between the mutual orientation of two contiguous individuals. Often however a great number of small crystals, — if they are even only rudimentary or embryonic (*trichites*, *crystallites*, etc.), — combine in a perfectly regular way according to definite laws. In such cases more or less symmetrical groupings result, of which the well-known *snow-crystals*<sup>1)</sup> (*fig. 132*) are most

1) G. Nordenskjöld, Bull. de la Soc. Minér. 16. 59. (1893); 17. 141. (1894); L. Bombicci, Bull. de la Soc. Minér. 3. 85. (1880).



beautiful examples, while the pretty *dendrites* exhibited by many substances when crystallising from a solvent, are closely related to the former, and known to all investigators who have studied crystallisation-phenomena through the microscope.

But even if the number of combining individuals is much smaller than in the cases mentioned, definite aggroupments of a few individuals frequently occur, which from a crystallographical point of view have certainly not less importance than the separate crystals referred to in the previous chapters.

If, in contrast with the special circumstances mentioned above,

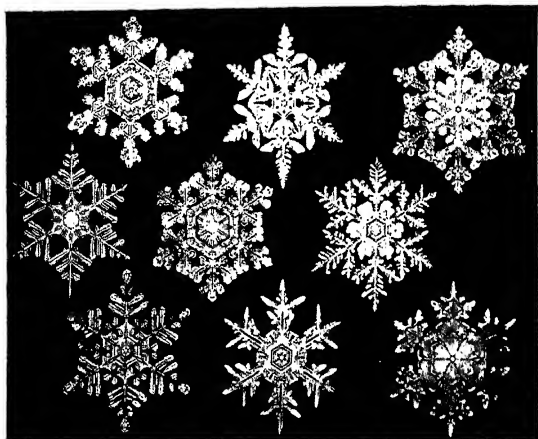


Fig. 132. Snow-Crystals.

crystallisation occurs in solutions which are only slowly moved, or if the process of crystal-formation is purposely retarded by increasing the viscosity of the solvent by the addition in minute quantities <sup>1)</sup> of gum or gelatine, — then between only a very small

<sup>1)</sup> O. Lehmann, *Molekularphysik I.* p. 415. (1888).

Here the aggregation-phenomena of crystals of *different* species are omitted; see for these interesting facts: F. Wallérant, *Crystallographie*, Paris, (1909). p. 491; J. Beckenkamp, *Statische und Kinetische Krystall-theorien I*, p. 187. (1913); Th. V. Barker. *Journ. Chem. Soc.* **89**. 1120. (1906); *Miner. Magaz.* **14**. 235. (1907); O. Mügge, *Neues Jahrb. f. Miner. Beil. Bd.* **16**. 335. (1903).

Moreover Grandjean (*Bull. de la Soc. Minér.* **39**. 164. (1916) was able to demonstrate that also the *fluid crystals* and *anisotropic liquids* of *p*-azoxyanisol, *p*-azoxyphenetol, anisaldazine, ethyl-*p*-azoxybenzoate, and ethyl-*p*-azoxycinnamate

number of individuals do particular aggregates make their appearance. These apparent associations of crystals are always the same and quite characteristic for the crystals under consideration. Their formation is governed by strict laws, and such "compound crystals" show a constancy of their interfacial angles and mutual orientation with a degree of perfection analogous to that which is met with in the properties of so-called single individuals.

Such apparent aggroupments consist always of two or more individuals of the same kind<sup>1)</sup>, every two of which are symmetrically arranged with respect to a net-plane or to a molecular row of the space-lattice. They are commonly distinguished as *twins*.

In the case of real twins, these are called a twin of the *first* order, if the symmetry-element of the compound crystal be a *row* of particles; if it is a *net-plane*, the twins are said to be of the *second* order.

Now the examples of these crystal-aggregates which have been longest studied, are just the rather simple, real *twins*. In quite early times a distinction was introduced between twins which appear to be formed by *juxtaposition* of the composing individuals, and those made by their *mutual penetration*. In the first case the molecular system of both individuals is considered to be symmetrical with respect to the plane of juxtaposition or *composition-plane*, — it may coincide with the proper twinning-plane or not (*gypsum*). This composition-plane may be parallel to the twinning-axis, or to the twinning-plane, or it may be perpendicular to one of them; but it must always be a possible crystallographical plane of the crystal, or a plane perpendicular to a crystallographically possible edge of it. The common straight line of both individuals may be a possible edge of the crystal, or the normal to a possible crystal-face.

Of course a symmetry-axis of *even* period or symmetry-planes of the crystal, can never have the functions of a twinning-axis or of a twinning-plane; for in that case not twins, but *parallel growths* of two crystals would be produced.

In the second case the molecular systems of the two individuals are, as it were, soldered together: the two crystals are symmetrical

take, as a rule, regularly oriented positions with respect to the crystallographical directions of cleavage-lamellae prepared from *muscovite*, *orpiment*, *zincblende*, *phlogopite*, *brucite*, *talc*, *leadhillite*, *sylvine*, *rock-salt* and *pyrophyllite*, if brought into immediate contact with them.

<sup>1)</sup> A. Sadebeck, *Angewandte Krystallographie*, p. 244 (1873); O. Lehmann, *Molekularphysik I.* p. 293—407. (1888).

with respect to a centre or a molecular row of the space-lattice, the direction of it being other than the axis of the constitutive particle itself, in the sense of Bravais' theory. (*fluorspar*; fig. 133). This is valid for holohedral, as well as for merohedral forms; in the first case however Mallard has shown that the sym-

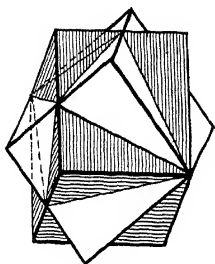


Fig. 133.  
*Fluorspar*. (Twin.)

metry-axis of the new compound crystal as a whole, can also be an axis of *approximate* symmetry of the space-lattice under consideration, in the sense in which we have defined it in the preceding chapter, and that a special tendency to the symmetrical arrangement of the separate individuals round this axis of approximate symmetry is observable in these cases<sup>1</sup>). In connection with this it must be remarked that such twins can also have a plane of symmetry, and in the case of holohedral crystals, a plane of approximate sym-

metry. This is easily understood if one considers that, if an axis of even period and an inversion-centre be the symmetry-elements of twins, the existence of a symmetry with respect to a plane perpendicular to that axis also is of course involved as a logical consequence.

Resuming we may say that experience has shown there is a remarkable tendency in merohedral crystals to twin-formation, in such a way that as preferential twinning-elements there appear such planes or such axes of even periods, as in the holohedral class of the same crystal-system have the function of true symmetry-planes or of true symmetry-axes (*pyrite*). The twins appear therefore as an approximation to the holohedral symmetry of the system to which the crystal belongs, and according to Haidinger, they may be given the name of *completion*-twins (*calamine*, *quartz*). And, secondly, experience teaches that planes and axes of *approximate* symmetry may have the function of twinning-elements too; in this

<sup>1</sup>) E. Mallard. *Ann. des Mines*. **20**. (1876); *Bull. de la Soc. Minér.* **8**. (1885); *Revue Scientifique*. (1887); Cf. also: A. Bravais, *Etudes Cristallographiques*, Paris, (1866), p. 248.

It may be understood, that twins are *single* individuals. If there be spoken here and in the preceding paragraphs, of *two* or *more* individuals which form "compound" twins, then this is simply a mode of speech, used for the purpose to help imagination.

case therefore the twinning-process may be considered also as a way of apparently increasing the existent degree of symmetry of the crystal under consideration (*jeldspars*). Finally the twinning plane may be perpendicular to a symmetry-plane of the composing individuals; the same subdivision of the different twins as in the previous cases may be made here also.

In general the classification of twins into such as are produced by juxtaposition or by penetration, may have certain advantages from a *practical* standpoint; from a theoretical point of view however it may be considered as somewhat too limiting, as for instance the individuals of a twin by juxtaposition may at least partially penetrate each other to some extent.

Moreover it may be remarked, that in a crystal-aggregate several laws of twinning are often expressed simultaneously, so that very complicated relations may be produced in such compound twins. If the same kind of twinning be several times repeated in the formation of a crystal-aggregate, *polysynthetic* twins are said to be produced when the twinning-plane remains parallel to itself, so that the alternate individuals of the whole complex are in parallel position. If this twinning-plane however changes its direction in the successive repetitions of the twinning-process, so-called *cyclic* twins will be produced. Of both kinds of twins the mineral *aragonite* presents well-known examples.

§ 3. It cannot be our purpose here to go into the details of twinning-phenomena in general, as this is a special chapter of pure crystallography. We have only in the following to consider certain cases of repeated twinning, — more particularly of penetration-twins, — between individuals of the same crystal-species, which show *approximate*, or *pseudo-symmetry*.

There are a number of substances, the crystal-forms of which show a more or less close approximation to forms of higher symmetry.

Thus if a tetragonal crystal, like *chalcopyrite*:  $\text{CuFeS}_2$ , has an axial ratio  $a : c$  very near to *unity* (here: 1 : 0,9857), the tetragonal crystal has evidently a space-lattice which closely approaches to that of a *cubic* crystal. *Chalcopyrite* shows sphenoidal hemihedrism, but the interfacial angle  $(111) : (1\bar{1}1)$  is here  $108^\circ 42'$ , while for a regular octahedron it would be  $109^\circ 28'$ . This mineral has therefore a tetragonal, but clearly *pseudo-cubic*, space-lattice.

The same is the case if a rhombic crystal has a prism-angle of nearly  $60^\circ$  or  $120^\circ$ ; in this case the vertical binary axis of the crystal

has the direction of an *approximately* hexagonal or trigonal axis of the space-lattice, and the rhombic crystal mentioned above is a real *pseudo-hexagonal* or *pseudo-trigonal* limit-form. If a monoclinic crystal has an angle  $\beta$  only slightly different from  $90^\circ$ , while moreover in its axial ratio  $a:b:c$ , one or two of the quotients are close to unity, the said monoclinic crystal has a space-lattice which is distinctly *pseudo-tetragonal* or *pseudo-cubic*.

Such *pseudo-symmetrical* crystals will often betray in their external habit a certain approximation to higher symmetrical forms: thus *rubidium-nitrate* has a strikingly simulative hexagonal aspect <sup>1)</sup>. Or they will have a definite set of gliding-, or of cleavage-planes which are nearly parallel to the faces of a crystalform with a higher symmetry.

Pseudo-symmetrical crystals therefore are such as closely simulate a higher symmetry than they really have; this higher symmetrical form is in many respects like an ideal model to which the proper symmetry of the crystal tends, without ever reaching it.

Now it is one of the most remarkable facts observed in inorganic nature, that such *pseudo-symmetrical* crystals exhibit a strong and undeniable tendency to increase their deceptive appearance yet more by repeated twinning and regular aggregation.

The new complexes thus produced are called *mimetic* forms; the phenomenon itself bears the name of *mimicry* <sup>2)</sup>. This mimicry is often so perfect that only a careful study of the optical and physical properties which reveal the true symmetry of the real molecular arrangement of the crystal, can show the true character of it. As therefore the optical properties are evidently often in discordance with the geometrical form exhibited by these mimetic crystals, they are said to manifest *optical anomalies*. To the discussion of these anomalies we shall return later on.

§ 4. Some instances may elucidate this occurrence of mimetic forms.

*Chrysoberyll* is a *beryllium-aluminate* of the composition:  $\text{BeO}, \text{Al}_2\text{O}_3$ .

The mineral is orthorhombic ( $a:b:c = 0,4701:1:0,8500$ ); but its space-lattice is obviously pseudo-hexagonal, as is proved i. a. by the fact that the angle  $(001):(0\bar{1}1)$  is  $60^\circ 13'$ . Now three

<sup>1)</sup> F. M. Jaeger, Zeits. f. Kryst. **43**. 588. (1907).

<sup>2)</sup> G. Tschermak, Lehrbuch der Mineralogie (1897), p. 91; O. Mügge, Neues Jahrb. f. Miner. Beil. Bd. **14**. 245. (1901); **16**. 335. (1903); P. Fischer, Dissertation, Göttingen, (1911); V. Goldschmidt, Zeits. f. Kryst. **43**. 353. (1907).

individuals will combine in such a way that they form a *trilling* after the plane (031), so that the apparently *hexagonal* complex of *fig. 134.* is formed. By suitable development of the component individuals the re-entrant angles will recede gradually more and more into the background; finally they become imperceptible, the aggregate is flattened towards the face  $a = (100)$ , and now an individual is produced which in its external aspect no longer deviates from a true hexagonal crystal. The facets of  $\{100\}$  commonly show a featherlike striation, as the last indication of the twinning-process which has led to the deceptive form of the crystal; but its mimetic character is immediately revealed by optical investigation: indeed the optical character, as a direct manifestation

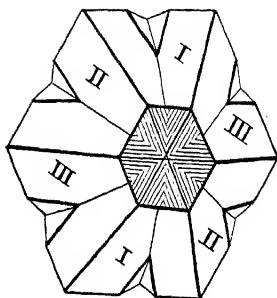


Fig. 134.  
*Chrysoberyll.*

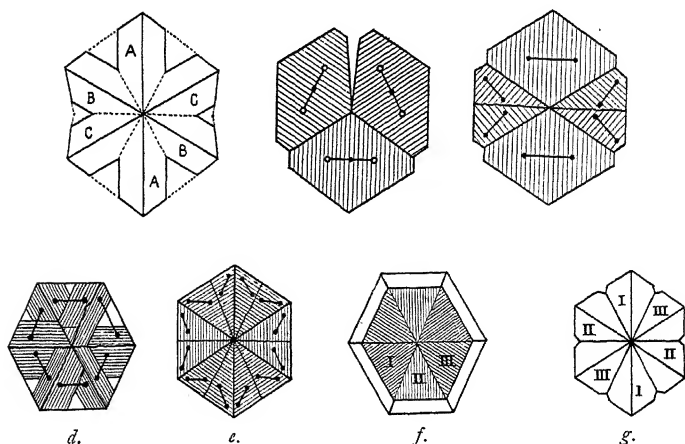


Fig. 135.

Basal sections of: *a, b, c:* Aragonite; *d:* Bromiite; *e:* Cerussite; *f:* Chlorite; *g:* Potassium-sulphate.

of its molecular structure, appears to be that of biaxial crystals.

In *fig. 135* basal sections are reproduced of some compound twins of *aragonite*:  $\text{CaCO}_3$ ; *witherrite*:  $\text{BaCO}_3$ ; *barytocalcite* or *bromiite*:

$\text{CaBa}(\text{CO}_3)$ ; *cerussite*:  $\text{PbCO}_3$ ; *chlorite*; *potassium-sulphate*:  $\text{K}_2\text{SO}_4$ ; etc.

*Aragonite* has a prism-angle of  $63^\circ 48'$ , and repeated twinning occurs with (110) as twinning-plane. The polysynthetic twins, especially when they are built up by fine lamellae, simulate a hexagonal or ditrigonal individual, but optical investigation easily proves that only a mimetic hexagonal-form of orthorhombic individuals is present.

*Witherite* occurs always in the shape of repeated twins which closely simulate hexagonal or ditrigonal individuals. The orthorhombic pseudo-hexagonal mineral has a prism-angle (110):  $(1\bar{1}0) = 62^\circ 12'$ ; the twins are usually very complex, the faces rough and striated.

The optical properties reveal the lower symmetry very clearly.



Fig. 136.  
*Cerussite*.

*Bromilite* (of *Bromley Hill*), *Cumberland*, the form of which is very nearly that of *witherite*, is found in dihexahedral pyramids formed by complex twinning; optical investigation shows that the simulative crystal is a combination of six individuals, as shown in the figure.

*Cerussite* has a prism-angle of  $62^\circ 44'$ ; the orthorhombic mineral forms apparently hexagonal twins (fig. 136), with the twinningplanes (110), and less often (130). They are optically biaxial, but their appearance is completely *ditrigonal*<sup>1)</sup>.

Another beautiful example of a pseudo-hexagonal substance is *potassium-sulphate*. The prism-angle (110) :  $(1\bar{1}0)$  is here  $59^\circ 36'$ ; repeated twins occur with (130) as twinning-plane, and the simulative effect is sometimes so great, that the crystals have wholly the aspect of true hexagonal bipyramids.

*Calcium-chloro-aluminate*<sup>2)</sup>:  $[\text{3CaO}, \text{Al}_2\text{O}_3, \text{CaCl}_2, 6\text{H}_2\text{O}] + 4\text{H}_2\text{O}$ , is monoclinic, with  $\beta = 87^\circ 13'$ , but pseudo-hexagonal, because the faces (310) and  $(3\bar{1}0)$  include an angle of about  $60^\circ$  with the plane of symmetry (010). Twinning occurs by three sets of lamellae, intersecting at  $120^\circ$ , and with (110) as twinning-plane; the crystals appear as thin hexagonal plates parallel to the apparent basal face (0001). At a temperature of  $36^\circ \text{C}$ . they become really rhombohedral and uniaxial.

<sup>1)</sup> Cf. also: J. Beckenkamp, *Zentralbl. f. Miner.* (1917), p. 25; O. Mügge, *Neues Jahrb. Beil. Bnd. 14.* 247 (1901).

<sup>2)</sup> G. Friedel, *Bull. de la Soc. Minér.* 20. 122. (1897); O. Mügge, *Neues Jahrb. f. Miner. Beil. Bnd. 14.* 264. (1901).

*Scolezite*:  $\text{CaAl}_2\text{Si}_3\text{O}_{10} + 3\text{H}_2\text{O}$  is monoclinic, with an axial ratio  $a:b:c = 0,9764 : 1 : 0,3434$ , and  $\beta = 98^\circ 18'$ . The prism-angle  $(110) : (\bar{1}\bar{1}0)$  is  $88^\circ 37\frac{1}{2}'$ . The space-lattice is therefore pseudo-tetragonal. Twins occur with  $(100)$  as twinning-plane; a section parallel to  $(001)$  shows the division in fields and strips, as drawn in *fig. 137*. (Lacroix).

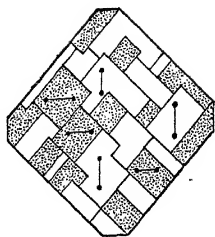


Fig. 137.  
*Scolezite*; section parallel  
to  $(001)$  (Lacroix).

How perfectly such crystals may approximate to real hexagonal or trigonal symmetry may also be seen from the stereographical projection of a Röntgen-pattern of *cerussite*, parallel to  $(001)$ , and obtained by us

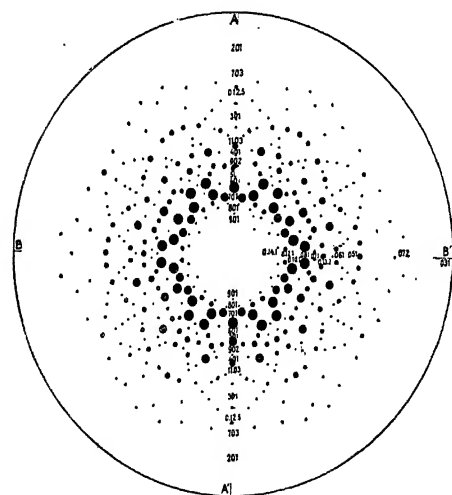


Fig. 138.  
Stereographical Projection of the Röntgen-pattern  
of *Cerussite*; plate parallel to  $(001)$ .

in our series of investigations of the symmetry of the Röntgen-patterns of isomorphously related substances<sup>1)</sup> in general. Although it is obvious, that the symmetry is only rhombic, it is remarkable how closely the image obtained approximates to that of a true hexagonal crystal (*fig. 138*).

§ 5. If repeated twinning occurs in several directions at the same time, compound penetration-twins of a very complicated structure may be

formed, and the approximation to higher symmetrical individuals obtained in this way may go remarkably far. As an instance of the

<sup>1)</sup> F. M. Jaeger and H. Haga, *Proceed. Kon. Akad. van Wet. Amsterdam*, 18. 1357. (1915).



way in which the approximation to the higher symmetrical form may take place, we here mention the mineral *phillipsite*, a zeolithic silicate of the composition:  $(Ca,K)Al_2(SiO_3)_4 + 4\frac{1}{2}H_2O$ .

This mineral is undoubtedly monoclinic; but its angle  $(110) : (1\bar{1}0)$  is  $60^\circ 42'$ , while  $(001) : (101) = 90^\circ 1'$ . It has therefore an approximate rhombic, as well as a pseudo-hexagonal symmetry. The result of the repeated twinning with  $(001)$  and  $(011)$  as twinning-planes, is a nearly square prism formed by four individuals, the faces of which are finally striated. Now three compound individuals of this kind may interpenetrate, with  $(\bar{1}10)$  as twinning-plane, to form a single yet more compound individual, as shown in *fig. 139*.

If the re-entrant angles be now gradually removed by the deve-

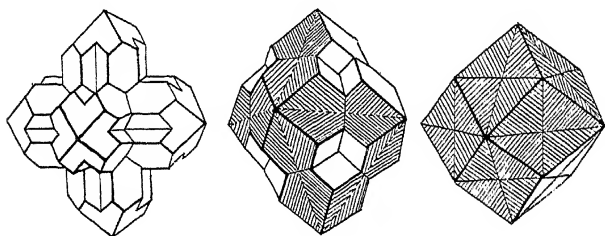


Fig. 139. *Phillipsite*.

lopment of the faces indicated, this complex of twelve crystals passes finally into the form of an apparent rhombicdodecahedron, as it is found in the cubic system. Each rhombic face of this may then be subdivided into four fields by striations diverging from the centre, and parallel to the position which would be occupied by one of the planes at each end of a ternary axis of the pseudo-dodecahedron thus obtained.

In general such remarkable mimetic forms are often met with in the group of the zeolithic silicates, a fact which may be connected in some way with the strange behaviour of these minerals with respect to their loss and absorption of water. Analogous phenomena as discussed here in the case of *phillipsite*, are found with *harmotome*, *stilbite*, etc., while the connection between the content of water and the occurrence of optical anomalies has been established beyond doubt in the case of *heulandite*, *chabazite*, *analcite*, etc., by the investigations of Mallard, Klein, Rinne, and others <sup>1)</sup>.

<sup>1)</sup> Cf. also: E. Mallard, *Ann. des Mines* **10**. 111. (1876); F. Becke, *Tscherm. Min. Mith.* **2**. 391. (1879); A. v. Lassaulx, *Zeits. f. Kryst.* **5**. 330. (1881);



bohedra just mentioned (*fig. 140a*). The angles of these extinction-directions with the diagonal of each rhombohedron-face will in these three cases be respectively:  $46^\circ$ , or  $11^\circ$ , or  $24^\circ$ .

The mimetic form thus obtained is therefore now an apparent rhombohedron, which however itself is again pseudo-cubic. Two such pseudo-cubic simulative forms may now combine into penetration-twins, with either their pseudo-trigonal axis  $c$  as twin-axis, or, rarely, with the face  $(10\bar{1}1)$  as twinning-plane.

In the first case we may have the complex of *fig. 140b*, which, by a suitable development of its bordering faces, finally obtains the simulative form of the regular rhombic-dodecahedron (*fig. 140c*), sometimes in combination with a subordinate form representing an apparent octahedron.

§ 6. The case of *chabazite* is very instructive in so far as it illustrates how strongly the tendency of the original lower symmetrical individual to simulate a higher symmetry, is exhibited. The triclinic individual has the latent predisposition in its space-lattice to imitate a trigonal symmetry; but it has also the capacity of simulating a yet higher symmetry, namely that of a cubic crystal. Now repeated twinning is made use of, first, to reach the already false position of a mimetic, pseudo-trigonal individual; but, as it were, not satisfied with this success, it again combines and recombines, until finally the deceptive form of the higher symmetrical cubic rhombic-dodecahedron is reached.

The result in all such cases is one of the same kind: the pseudo-symmetrical crystal finally approaches more closely, by repeated combination of individuals of its own species, to the higher symmetry, to which the predisposition is a part of its special internal structure, and of which the single individual is only a defective representative.

This strong tendency to strive at higher perfection by aggregation is one of the most remarkable facts in inorganic matter; it is a "struggle for higher symmetry", by the aid, as it were, of the most primitive form of "communism". Just as union into well-governed states gives a greater stability of life to human creatures, and is the necessary condition for their speedy and regular progress, so the aggregation of imperfectly shaped crystals into higher symmetrical complexes, is probably a way of reaching a higher degree of mechanical stability.

§ 7. It was such facts as these, that have led Mallard since 1876 to his most suggestive explanation of a number of optical

phenomena exhibited by numerous crystalline substances, namely the occurrence of the above mentioned *optical anomalies* and the *rotatory power in uniaxial crystals* belonging to the trigonal, tetragonal, and hexagonal systems.

Optical anomalies have been observed in a gradually increasing number of crystals ever since Brewster <sup>1)</sup> in the beginning of the nineteenth century first discovered and studied them. More especially the symmetry of the optical behaviour of such crystals appeared to be appreciably *lower* than that of their external forms; or, what is another view of the same fact: their geometrical form is evidently higher symmetrical than that of their internal molecular structure.

Thus many crystals of the cubic system are birefringent, and, in striking contrast to what might be expected, they act powerfully upon transmitted polarised light; tetragonal and hexagonal crystals are notoriously biaxial, and show optical phenomena analogous to those to be expected in rhombic, monoclinic, or triclinic crystals; etc.

The apparently cubic minerals: *boracite*, *leucite*, *perowskite*, *fluor-spar*, *diamond*, *garnet*, *analcite*, etc., are in most cases distinctly birefringent, and the same is true for many laboratory-products, such as *alums*, the *nitrates* of *barium*, *strontium*, and *lead*, *Schlippe's salt*, *sodium-chlorate*, *sodium-bromate*, etc., all crystallising in one of the classes of the cubic system. The apparently tetragonal crystals of *potassium-ferrocyanide*, of *strychnine-sulphate* etc., and of minerals like *idocrase*, *apophyllite*, etc., are beyond all doubt optically biaxial. The same is true for a great number of substances which, with respect to their crystal-forms, must belong to the trigonal or hexagonal systems, as for instance: *quartz*, *tourmaline*, *chabazite*, *sodium-periodate*, *beryll*, *apatite*, the *dithionates* of *potassium*, *rubidium*, *caesium*, *calcium*, *strontium*, and *lead*, and many other chemical compounds.

The disparity between the optical character of such crystals and their geometrical appearance is therefore an indisputable fact, and one even of frequent occurrence; and a very great number of highly interesting investigations have been made with the purpose of elucidating the causes of this striking discordance. The work done in this field has chiefly led to two different standpoints in the explanation of the phenomena considered. One class of investigators regards

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<sup>1)</sup> D. Brewster, Phil. Trans. London, *I.* 187. (1814); Trans. R. Soc. Edinb. *8. I.* 155. (1817); Phil. Trans. London, *I.* 199. (1818); Trans. R. Soc. Edinb. *9. I.* 139. (1821); *II.* 317. (1823); *10.* 187. (1826); Edinburg Phil. Journ. *1. 1.* (1819); *3.* 98. (1820); *5.* 217. 218. (1821); Phil. Mag. *7.* 245. (1835); etc.

the external form as the decisive and essential criterion for attributing the right degree of symmetry to the crystal; and the discordance between this symmetry and that of the optical phenomena observed is explained by them by the supposition of the influence of secondary, disturbing forces, like internal tensions produced by isomorphous admixture, by rapid cooling, by changes in volume as a consequence of polymorphic transformations, etc. The other view is that the optical properties reveal the true character of the space-lattice of the crystal, and therefore of the true symmetry of the molecular arrangement itself, while the external form is only to be considered as a simulated, a mimetic one, exhibiting only an *apparent* symmetry. According to the first view, the disparity mentioned above may really be considered as an occurrence of "optical anomalies", while according to the second, it is reduced rather to a case of "geometrical anomalies" than to one of optical deviations. To the adherents of the views first mentioned, objects of this kind are higher symmetrical than they appear to be from their optical behaviour; for the supporters of the last mentioned views, these crystals appear higher symmetrical than they really are. In the first case we should have to look on them as on human beings who, by a combination of unfavorable circumstances, are forced to show themselves in a degenerate state and worse than they ought to be; in the second case we should have to regard them more as we should a servant, who dressed himself in the clothes of his master and with the external signs of his dignity, giving himself the ridiculous appearance of an individual whose exterior is in flagrant contrast with his inner inferiority. If this matter might be looked at in this anthropomorphic way, the whole existence of these strange individuals would have to be considered in the first case as an almost tragical fact, in the second rather as a caprice of nature full of humour.

§ 8. On the other hand, the *explanation of the rotatory power of uniaxial crystals* first discovered by Biot, has not been given in any satisfactory way since the development of the optical theory of that phenomenon by Fresnel. The latter had made the supposition, that the propagating rectilinear ray consisted in reality of two equal circularly polarised rays with opposite rotation-directions, of which the one traversed the crystal with a greater speed than the other. The result of this difference in velocity is a difference in phase, and if the action of both rays on leaving the crystal be again combined, a deviation of the original plane of polarisa-

tion, either to the right or to the left, must necessarily occur.

This conception is however more a description of the phenomenon than an explanation, because it includes no rational cause, either why the one ray should be retarded in the crystalline medium with respect to the other, or why the phenomenon, so far from being a general one for such uniaxial crystals, is on the contrary a relatively rare one.

The famous experiment of Von Reusch <sup>1)</sup> in 1869, who succeeded in exactly imitating the phenomenon of the rotatory power in uniaxial crystals by the regular piling up of a great number of biaxial laminae of mica crossing under angles of 45° and 60°, gave a first indication in which direction a solution of the problem might be looked for. In point of fact the theory of the optical effect of such piles of lamellae was developed in its base outlines by Sohncke <sup>2)</sup>, and more fully by Mallard <sup>3)</sup> in 1876, while a great number of experimental investigations, among others those of Wyruboff <sup>4)</sup> regarding the properties of the crystals of *quartz*, *cinnabar*, *potassium-rubidium-*, *calcium-*, *strontium-*, and *lead-dithionates*, *strychnine-sulphate*, *strychnine-selenate*, *diacetyl-phenol-phtaleine*, *benzile*, *ethylene-diamine-sulphate*, *guanidine-carbonate*, *sodium-chlorate* and *-bromate*, of some *uranyl-double-acetates*, and of several other substances, have strikingly confirmed the correctness of these views in a great number of cases.

One of the most beautiful examples of this kind is unquestionably the *ammonium-lithium-sulphate*:  $(\text{NH}_4)\text{LiSO}_4$ , described by Wyruboff <sup>5)</sup>, the crystals of which are endowed with a strong rotatory power

<sup>1)</sup> E. von Reusch, Pogg. Ann. der Phys. **138**. 628. (1869).

<sup>2)</sup> L. Sohncke, Pogg. Ann. der Phys. Ergänzt. Bnd. **8**. 16. (1876).

<sup>3)</sup> E. Mallard, Ann. des Mines (7). **10**. 119. (1876); *ibid.* (1881).

At my request, professor Lorentz in 1905 was kind enough once more to treat theoretically the problem of the optical effect of a pile of regularly arranged, infinitely thin, biaxial lamellae. The result of his very general reasonings is a qualitative agreement with the results obtained by Mallard, while quantitatively there are some differences in the final values for the rotation-angle. In every case the theory of the superposed lamellae may certainly be regarded as based upon a perfectly sane supposition.

<sup>4)</sup> G. Wyruboff, Ann. de Chim. et Phys. (6). **8**. 340. (1886); Bull. de la Soc. Minér. **7**. 10, 49, 86. (1884); Cf. also: A. Bodländer, Inaug. Dissert. Breslau, (1882); F. Klocke, Neues Jahrb. f. Min. **2**. 97. (1880); C. Pape, Pogg. Ann. **139**. 229. (1870); W. Barlow, Zeits. f. Kryst. **27**. 468. (1896).

<sup>5)</sup> G. Wyruboff, Bull. de la Soc. Minér. **13**. 217. (1890).

If an individual be studied composed of several intergrown lamellar crystals (*fig. 141*), local triangular spots are met with, consisting

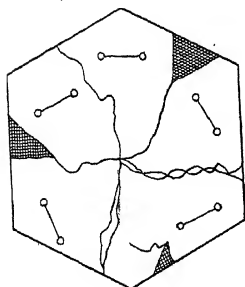


Fig. 141.  
Basal section of  
*Ammonium-lithium-sulphate*.

of lamellae interwoven at angles of  $60^\circ$ , which become extinguished between crossed nicols in any situation; but these are just the parts endowed with rotatory power. There cannot be the least doubt here, that the rotatory power of these parts is governed by the crossing of the biaxial laminae, in full accordance with Mallard's theory.

In general it has become clear from these researches, that a great number of crystals showing *optical rotatory power* also exhibit *optical anomalies* in the sense indicated above, and that these

dextro-, or laevogyrotatory uniaxial crystals, are in reality all very complicated twins of lower symmetrical material. They are therefore true *pseudo-symmetrical* crystals, built up according to definite twinning-laws, by a great number of biaxial *lamellae*, which in an analogous way to that demonstrated in the cases of *phillipsite* and *chabazite*, combine into an apparently higher symmetrical, "mimetic" aggregate. The special circumstances of crystallisation seem to have a certain influence on the arrangement of the composing lamellae, so that within certain limits a fluctuation of the optical properties of such crystals may evidently occur. The inconstancy of the magnitude of the rotatory power of such crystals was in many cases confirmed by direct observations.

§ 9. Now Mallard, basing his theory on the observed fact that the crystals which show optical anomalies are just those whose geometrical properties are closely approximate to those of higher symmetry, considers the optically anomalous crystals as without exception *pseudo-symmetrical aggregates* of lamellae, the space-lattice of which has a lower degree of symmetry than the crystal as a whole possesses.<sup>1)</sup> If for instance (*fig. 142*) a rhombic crystal has a space-lattice, the layers of which, parallel to the plane of drawing,

<sup>1)</sup> E. Mallard, *Explication des Phénomènes Optiques Anomalous dans les Substances Cristallisées*, Paris, 1876; *Ann. des Mines* (7). 10. 60. (1876); *Bull. de la Soc. Minér.* 5. 144, 214. (1882); 7. 349. (1884); A Scacchi, *Zeits. der deutschen Geol. Ges.*, (1864), p. 35.

consist of particles arranged in rhomboids of *nearly*  $60^\circ$ , then the binary axis of the rhombic individual perpendicular to the plane of this layer is at the same time an axis of *apparently threefold symmetry*. Thus, if the space-lattice be turned round this axis of apparent symmetry through  $120^\circ$  or  $240^\circ$ , the space-lattice in its new positions will coincide, *not completely*, it is true, but in any case *very nearly*, with the space-lattice in its original position.

If therefore such layers of molecular dimensions are successively subjected to all symmetrical operations which correspond to the presence of one or more symmetry-elements of *apparent symmetry* in the space-lattice under consideration, a complex pseudo-symmetrical crystal may be formed, exhibiting rotatory power or not, according to the way in which the superimposed layers are arranged.<sup>1)</sup>

As the cross-laid lamellae become thinner, and their compound twinning and mutual penetration more perfect, the mimetic crystals will approach more closely to a true higher symmetrical individual; and if the dimensions of the transverse lamellae become submicroscopically small, the crystal is no longer distinguishable from a homogeneous one by any existing physical means. Mallard then says that the substance under consideration is *dimorphic*; the symmetry of both polymorphic forms being that of the composing lamellae on the one hand, and that of the higher symmetrical individual now obtained on the other. The higher symmetrical modification thus appears as an extremely perfect and regular aggregate of submicroscopical individuals of the lower symmetrical form, — in an analogous way to that in which the mixed-crystals are built up from their isomorphous components by the intercalation of alternating layers of molecular dimensions.<sup>2)</sup>

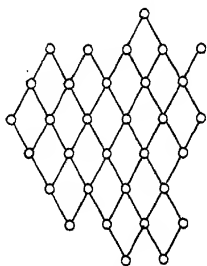


Fig 142.

The suggestive idea of Mallard therefore should have the great advantage of reuniting under the same point of view *three* different phenomena exhibited by crystals: their *optical rotatory power*, their *optical anomalies*, and their eventual *polymor-*

1) If, for instance, the angle between the consecutive lamellae be  $90^\circ$  or  $180^\circ$ , no rotation of the plane of polarisation of the emergent ray will occur.

2) See however in this respect: L. Vegard and H. Schjelderup, *Phys. Zeits.* 18. 93. (1917).



*phism*. They should all be explained by the repeated twinning of pseudo-symmetrical space-lattices and their combination into aggregates of apparently higher symmetry<sup>1</sup>).

§ 10. It may be asked if any indication of such lamellar structure in crystals showing optical anomalies, is really found? Experience has indeed plainly established its existence, as by some more detailed examples may be demonstrated in the following.

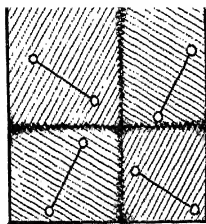


Fig. 143.  
Potassium-ferrocyanide.  
Plate parallel to (010).

One of the instances of this kind most studied<sup>2</sup>) is *potassium-ferrocyanide*:  $K_4\{Fe(CN)_6\}$ , the optical anomalies of which were discovered by Brewster. The crystals are monoclinic, but they are so nearly tetragonal, that for a long time they were considered really to belong to the last mentioned system.

Indeed the axial ratio is:  $a : b : c = 0.3947 : 1 : 0.3983$ , with  $\beta = 90^\circ 1'$ ; from these numbers the approximate tetragonal character of the space-lattice is immediately clear.

The optical properties are those of a biaxial crystal; the rather large angle of the optical axes is about  $120^\circ$  for sodium-light, and the character of birefringence is positive. In compound crystals a plate parallel to the planes of  $\{010\}$  appears between crossed nicols to be divided into four sectors (fig. 143), two of them diametrically opposed of negative, the other two of positive character. The boundary-lines of the fields are parallel to the edges of the quadratic plates. In every two adjacent sectors the planes of the optical

<sup>1</sup>) That this explanation of "polymorphism" cannot always hold, is evident, as has already been recognised by Mallard himself. The mere difference in *specific weight* between the two modifications, as it is observed frequently, cannot be plausibly explained by his theory. However there is a certain number of substances which behave just as Mallard's view demands. At present these substances are classified as those, which are *pseudo-symmetrical*, to distinguish them from those in which true *dimorphism* occurs. Cf. P. Groth, *Einleitung in die Chemische Krystallographie*, (1904), p. 4—7; G. Wyruboff, *Bull. de la Soc. Minér.* **29**. 335. (1906); F. Wallérant, *ibid.* **24**. 159. (1901); **27**. 184. (1904).

<sup>2</sup>) G. Wyruboff, *Ann. de Chim. et Phys.* (4). **16**. 293. (1869); **29**. 335. (1906); R. Brauns, *Die optischen Anomalien*, (1891); p. 58; G. W. Wulff, *Verh. der Kais. russ. Miner. Ges. Petersburg*, (2). **29**. 65. (1892); A. Karnojitzki, *Zeits. f. Kryst.* **19**. 571. (1891); *Russ. Berg-Journ.* (1892) No. 10; *Ref. Zeits. f. Kryst.* **24**. 512. (1895).

axes are perpendicular to each other; all four sectors become simultaneously dark between crossed nicols, if the sides of the quadratic plate include an angle of about  $34^\circ$  or  $56^\circ$  respectively, with the planes of vibration of polarizer and analyser.

The whole behaviour of these crystals is in full agreement with the supposition that they are composed by monoclinic lamellae, crossing at  $90^\circ$ , and intercalated in such a way that an apparently tetragonal crystal is produced. There cannot be the least doubt as to the correctness of Mallard's view in this case.

The same is valid for the case of *autunite* <sup>1)</sup>:  $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 + 8\text{H}_2\text{O}$ , ( $a : b : c = 0,3463 : 1 : 0,3525$ ;  $\beta = 90^\circ 30'$ ); of *natrolithe*:  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} + 2\text{H}_2\text{O}$ ; of *prehnite* <sup>2)</sup>:  $\text{CaH}_2\text{Al}_2\text{Si}_3\text{O}_{12}$ ; of *penmine* <sup>3)</sup>:  $2$  or  $3$  ( $\text{Mg}_3\text{H}_4\text{Si}_2\text{O}_9$ ) +  $\text{Mg}_2\text{H}_1\text{Al}_2\text{SiO}_9$ ; and of some other substances which even by Brauns, who in general does not agree with Mallard's views, are considered to be true mimetic aggregates of lower symmetrical lamellae.

The cases of the pseudo-cubic minerals *boracite*:  $\text{Mg}_7\text{Cl}_2\text{B}_{16}\text{O}_{30}$ , and *leucite*:  $\text{KAlSi}_2\text{O}_6$ , as optically anomalous crystal-species, are well-known, and a great number of investigations has already been made with respect to these remarkable substances. In especial the work of Mallard and C. Klein has much contributed to the explanation of their abnormal behaviour <sup>5)</sup>. Without going into details, we may mention here that in both these cases the lamellar structure is beyond all doubt.

In *fig. 144* a crystal of *leucite* with its typical striation of the apparent icosahedron-faces is reproduced, and the aspect of a plate parallel to the cube when observed between crossed nicols. The

<sup>1)</sup> A. Brezina, Zeits. f. Kryst. **3**. 273. (1897); A. Madelung, *ibid.* **8**. 75. (1884); R. Brauns, *loco cit.* p. 63.

<sup>2)</sup> C. Stadtländer, Neues Jahrb. f. Miner. (1885); *II*. p. 113; A. Von Koenen, Sitzber. d. Ges. zu Beförd. d. Naturwiss. Marburg, (1874); R. Brauns, *loco cit.*

<sup>3)</sup> A. Des Cloizeaux, Bull. de la Soc. Minér. **5**. 58, 125. (1882); E. Mallard *ibid.* p. 70, 195. (1882); R. Brauns, *loco cit.* p. 69.

<sup>4)</sup> R. Brauns, Die Optischen Anomalien, (1891), p. 74.

<sup>5)</sup> E. Mallard, Ann. des Mines (7). **10**. 79, 93. (1876); Bull. de la Soc. Minér. **2**. 147. (1879); **5**. 144, 216. (1885); E. Mallard and H. Le Chatelier, *ibid.* **6**. 122. (1883); **6**. 129. (1883); **9**. 69. (1886); C. Klein, Neues Jahrb. f. Miner. (1880) *II*. p. 209; (1888) *I*. p. 239; Gött. Nachrichten, (1881); (1884); p. 189, 421; Neues Jahrb. f. Miner. (1884) *I*. p. 235; *II*. p. 49. (1887). *I*. p. 224, 234. (1885) Beil. Bnd. *III*. p. 522; R. Brauns, *loco cit.* p. 88, 106, (1891) H. Baumhauer, Zeits. f. Kryst. **1**. 257. (1877); etc.

lamellae disappear abruptly at about  $500^{\circ}\text{C.}$ , and re-appear on cooling.

Of *boracite* in *fig. 145* a plate parallel to (111) in its condition after heating and subsequent cooling has been reproduced (Mallard),

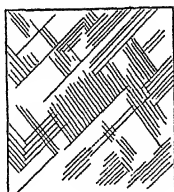
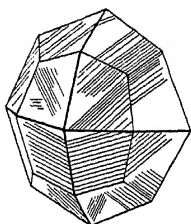


Fig. 144.  
*Leucite.*

which shows the lamellar structure quite clearly. At  $265^{\circ}\text{C.}$  the birefringence disappears suddenly, and re-appears without retardation if the crystal be cooled down below that temperature. The optical behaviour of plates cut

parallel to (110) and (100) is schematically shown in *fig. 146*, while in *fig. 147* a pseudo-rhombicdodecahedron of *boracite* is reproduced, and the arrangement of the component rhombic individuals is indicated by the direction of their axial plane. Every face of the rhombicdodecahedron is the base of a rhombic pyramid, with its top lying in the centre of the crystal; the biaxial individuals have their optical axial plane parallel to the longer diagonal of each rhomboid. By means of Röntgen-rays, patterns for plates parallel to (100), (110), and (111) were obtained by us<sup>1)</sup> at room-temperature, which were in accordance with the symmetry of a cubic space-lattice, but also others which, when parallel to (100), only manifested a binary axis with two perpendicular planes of symmetry; the last plate however, when heated to  $300^{\circ}\text{C.}$ , and then passed by a pencil of Röntgen-rays, gave a pattern, the symmetry of which was that of a true cubic crystal-plate.

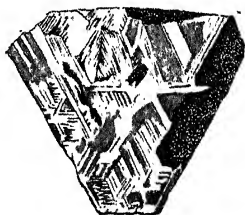


Fig. 145.  
*Boracite.*  
Plate parallel to (111).

Although definite conclusions cannot yet be drawn from these results, the last mentioned experiment nevertheless seems to support the explanation given by Mallard. In the case of *leucite* we were not able to obtain Röntgen-patterns at all, whose symmetry was

<sup>1)</sup> H. Haga and F. M. Jaeger, *Proceed. Kon. Akad. van Wet. Amsterdam*, vol. 16, (1914).

in accordance with a cubic space-lattice; here indeed no such cubic lattice seems to be present, but instead of this rather a very complicated arrangement of lower symmetrical individuals.

As far as we can at present judge, the behaviour of *leucite*-crystals

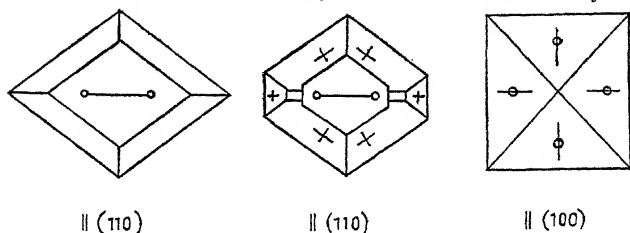


Fig. 146.

*Boracite.*

Plates parallel to (100) and (110).

towards Röntgen-radiation, can surely not be explained by the mere assumption of internal stresses which are related to the limiting facets and edges of the crystals.

In the same way in *fig. 148—153*, several other crystal-sections are drawn, as they appear between crossed nicols. Here the optical properties of plates cut from crystals of *garnet*, parallel to (110); of *analcite*, parallel to (100); of *fluorspar*, parallel to (110); of *perowskite*, parallel to (100) and (111); of *apophyllite*, parallel to (001) and at 45° to the planes of the nicols; and of *rutile*, parallel to (001) are expressed, as observed by Mallard and others.

In particular the figure relating to *perowskite*:  $\text{CaTiO}_3$ ; parallel to (100), is very instructive. There is not the least doubt in this case that we have here to deal with a pseudo-cubic crystal, being in reality a very complex twin of differently oriented lamellae. According to Baumhauer<sup>1)</sup>, and Von Kokscharow<sup>2)</sup>, the true

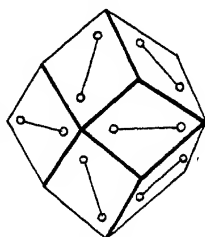


Fig. 147.

*Boracite.*

1) H. Baumhauer, Zeits. f. Kryst. 4. 187. (1880).

2) N. Von Kokscharow, Materialien zur Mineralogie Russlands, Bnd. 6, p. 388. (1871); 7. p. 375. (1875); 8. p. 39. (1878); Neues Jahrb. f. Miner. (1878), p. 38; A. Ben Saude, Ueber den Perowskit, Göttingen, (1882); C. Klein Neues Jahrb. f. Miner. (1884). I. p. 245; A. Des Cloizeaux, Neues Jahrb. f. Miner. (1875), p. 279; (1877), p. 160, 499; (1878), p. 43; Ann. des Mines (5). 14. 417. (1858); Pogg. Ann. 126. 420. (1865).

symmetry should be orthorhombic, with a twinning chiefly occurring with respect to a face of the prism  $\{110\}$  and of the pyramid  $\{111\}$ .

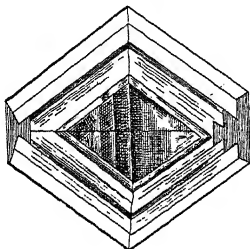


Fig. 148.  
*Garnet*; section parallel to (110).

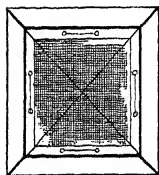


Fig. 149.  
*Analcite*; section parallel to (100).

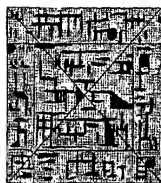


Fig. 150.  
*Fluorspar*; section parallel to (100) and (111).

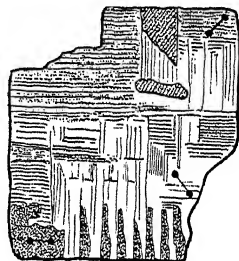
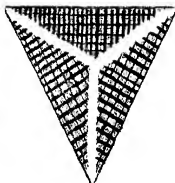


Fig. 151.  
*Perowskite*; section parallel to (100).

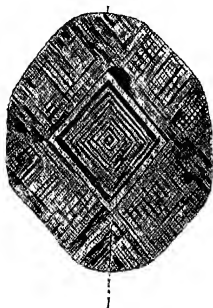


Fig. 152.  
*Apophyllite*; section parallel to (001).

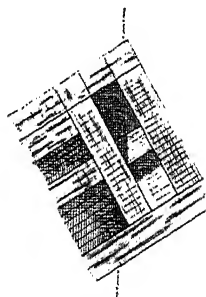


Fig. 153.  
*Rutile*; section parallel to (001).

In several of these cases, Brauns and others have tried to demonstrate that the optical anomalies are caused by internal stresses,

as a consequence of isomorphous admixture, etc.; cf.: Brauns, loco cit., p. 358, (1891). The truth may lie in the middle in this matter too, the two views separately being perhaps both too exclusive and one-sided. It is quite possible and even probable, that in many cases internal stresses are in fact the direct cause of the optical anomalies; but our experience in the study of the anomalous crystals by means of Röntgen-rays seems to indicate, that there is in many cases a greater probability of the correctness of Malard's view.

In the course of our studies on the symmetry of the

Röntgen-patterns in general<sup>1)</sup>, a series of optical anomalous crystals were also investigated: besides *boracite* and *leucite* already mentioned, *po-*

*tassium-ferrocyanide*, *apophyllite*, *sodium-chlorate*, *benitoite*, *racemic tri-ethylenediamine-cobalti-bromide*, *benzile*, *brucite*, etc. were studied, and also some crystals endowed with rotatory power, like *quartz*, *cinnabar*, *strychnine-sulphate*, etc. Although in the last mentioned cases faultless patterns were obtained (fig. 154), — a fact which demonstrates to what high degree of perfection this supposed lamellar intercalation can go, — we observed in the case of *apophyllite*, *potassium-ferrocyanide*, *benzile*, *benitoite*, and the complex *cobalti-salt* just mentioned, that even from apparently homogeneous and faultless plates, patterns of a lower symmetry were obtained, than should be the case with respect to their proper symmetry.

In particular, images were obtained which possessed only a single

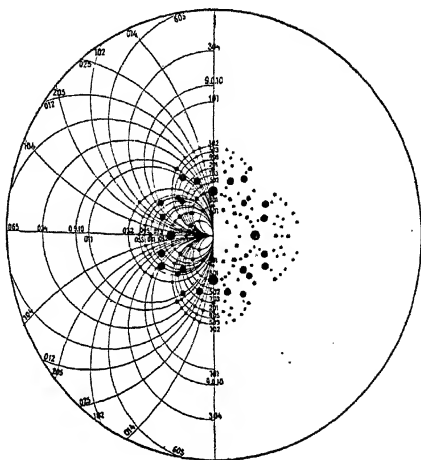
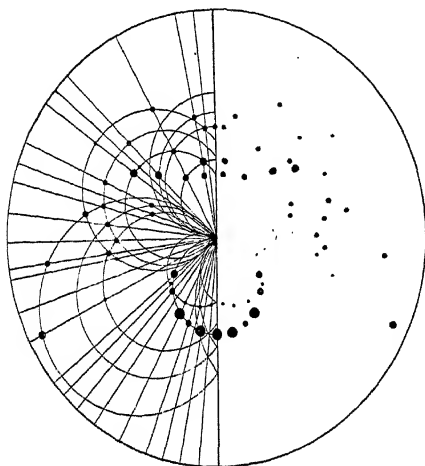


Fig. 154.  
Stereographical Projection of the Röntgen-pattern  
of pseudo-tetragonal *Strychnine-sulphate*.

<sup>1)</sup> Cf. H. Haga and F. M. Jaeger, *Proceed. Kon. Akad. v. Wet. Amsterdam*, Vol. 16, 17, 18, (1914—1916); 17. 438. (1914); 18. 1355, 1552. (1915).

plane of symmetry, as is quite normal for monoclinic crystals cut parallel to (100) or (001), or to any other face of the orthodiagonal-zône<sup>1)</sup>. As an instance of this in fig. 155 the Röntgen-pattern, as it was obtained with racemic *tri-ethylenediamine-cobalti-bromide* is



155.

Stereographical Projection of an abnormal Röntgen-pattern of the pseudo-tetragonal  
*rac.-Tri-ethylenediamine-Cobalti-bromide*.

reproduced in stereographical projection.

Here the natural crystals parallel to (001) were used in the experiment<sup>2)</sup>, in the shape of very thin, splendidly developed pseudo-hexagonal plates which showed an exactly central and almost undisturbed axial image in convergent polarised light; a slight deformity of the axial interference-image, because of an apparent biaxiality of the substance,

was the only abnormality observed. Analogous phenomena were met with in the case of the perfectly transparent *benzile*-plates cut parallel to (001), and of cleavage-lamellae of *apophyllite*<sup>3)</sup>. *Potassium-ferrocyanide* once gave an almost tetragonal-symmetrical pattern, but in most cases abnormal images showing only a single plane of symmetry. Obviously this is a fact which supports the lamellar theory; for it proves that local disturbances of the structure occur, which cannot but consist of a slight rotation of a part of the basal plate round an axis having the direction of the perpendicular to the plane of symmetry visible in the obtained pattern. If such a crystal be composed of lamellae, it is easily conceivable that such dislocations may occur, if a pile of lamellae is rotated round its longer

1) F. M. Jaeger, *Proceed. Kon. Akad. van Wet. Amsterdam*, **18**. 51. (1915).

2) H. Haga and F. M. Jaeger, *ibid.* **18**. 1201. (1915).

3) H. Haga and F. M. Jaeger, *ibid.* **17**. 438. (1914).

direction a little bit. The effect will depend on the accidental choice of the place where the pencil of Röntgen-rays pierces the crystal-plate, as was in fact stated in some cases <sup>1)</sup>. As stress or tension produced in the plate by slightly compressing it, has no appreciable effect, as long as the crystal be not internally dislocated by the force applied, the phenomenon mentioned here can only be caused by a local disarrangement of some of the component lamellae. In the opinion of the present writer, therefore, there is scarcely room for doubt that the explanation given by Mallard will prove to hold in the larger number of cases <sup>2)</sup>.

§ 11. At present however the explanation given by Mallard for the phenomenon of *dimorphism* can scarcely be maintained.

The study of polymorphism in recent times has proved beyond all doubt, that in the case of *reversibility* of this phenomenon, i. e. if true *enantiotropy* be present, we have in reality to deal with a true heterogeneous equilibrium between two different phases, which under any given pressure is determined by a definite temperature, generally called the *transition-temperature*. Above this temperature the one modification is the stabler one, below it the other form; and if no retardation-phenomena occur, the transformation of the one form into the other occurs *abruptly*, with a specific *heat-effect* and a change of specific volume. Now in Mallard's explanation of dimorphism, such an abrupt change, accompanied by an appreciable heat-effect, would be hardly conceivable. For if the higher symmetrical form were nothing but a mimetic aggregate of submicroscopical, repeatedly twinned lamellae of lower symmetry, that higher symmetrical form would, from a thermodynamical standpoint, represent in fact *the same phase* as the lower symmetrical modification by which it is composed. Therefore one would expect that the change would neither be accompanied by a considerable heat-effect, nor by an abrupt transition, but rather by a gradual transformation, because the component lamellae, according to Mallard's view, get gradually finer and finer with increase of temperature. In practice this trajet may be larger or smaller, and the change may occasio-

1) H. Haga und F. M. Jaeger, loco cit.; e. g. in the case of *d-sodium-ammonium-tartrate*, parallel to (010).

2) G. W. Wulff, Zeits. f. Kryst. 17. 592. (1890); G. Wyrouboff, Bull. de la Soc. Minér. 8. 78, 398. (1885); 13. 213, 277. (1890); 14. 215, 233. (1891); Ann. de Chim. et Phys. (6). 8. 340. (1886); etc.; F. Wallérand, Bull. de la Soc. Minér. 24. 155. (1901); 27. 184. (1904).



nally even give the impression of occurring suddenly. Indeed, as far as experience goes, the change of apparently symmetrical substances into the higher symmetrical forms, even when it seems to take place instantaneously, is never accompanied by an appreciable heat-effect, nor by a measurable change of specific volume.

A study of these phenomena from these points of view has been made in several very convincing cases. Thus the temperature at which the monoclinic, pseudotrigonal *uranyl-magnesium-sodium-acetate*<sup>1)</sup>:  $\text{NaMg}(\text{UO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_9 + 9\text{H}_2\text{O}$  is changed into an apparently-real trigonal crystal, was determined to be 28° C. by Steinmetz, who stated at the same time that the change observed is accompanied neither by an appreciable dilatometrical, nor by a thermal effect.

Analogous results were obtained by Steinmetz with *isopropylamine-platini-chloride*<sup>2)</sup>:  $(\text{iso-} \text{C}_3\text{H}_7.\text{NH}_2)_2\text{PtCl}_6$ , which is a monoclinic, but pseudo-rhombic substance, and which at 32° C. is changed into an apparently-true rhombic individual, without measurable heat-, or volume-effects. Something of the same kind was found by Gossner<sup>3)</sup> in the case of *glaserite*:  $\text{K}_3\text{Na}(\text{SO}_4)_2$ , and of the corresponding *chromate*:  $\text{K}_3\text{Na}(\text{CrO}_4)_3$ ; here too, neither heat- nor volume-effects were found when the monoclinic, pseudo-hexagonal crystals passed into such of apparently-true hexagonal symmetry.

Beautiful examples were also found by Gossner<sup>4)</sup> in the case of the *tri-alkali-hydrosulphates*:  $\text{K}_3\text{H}(\text{SO}_4)_2$ ,  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ , and  $\text{Ti}_3\text{H}(\text{SO}_4)_2$ , and in that of the corresponding *selenate*:  $\text{K}_3\text{H}(\text{SeO}_4)_2$ . The *ammonium*-, and *potassium-hydrosulphates* are monoclinic and pseudo-trigonal; the *thallo-salt* is really ditrigonal, with approximately the same angular values. On heating the monoclinic salts, a system of three sets of lamellae, crossing at an angle of 60°, becomes visible, which at increasing temperatures get gradually more numerous, until finally an apparently-perfect ditrigonal crystal is produced. The transformation is completely reversible, and according to Gossner a continuous one. Fischer<sup>5)</sup> however demonstrated

1) G. Wyrouboff, Bull. de la Soc. Minér. **24**. 93. (1901); Zeits. f. Kryst. **37**. 192. (1903).

2) A. Ries, Zeits. f. Kryst. **36**. 329, 360. (1902); H. Steinmetz, Zeits. f. phys. Chemie, **52**. 449. (1905).

3) B. Gossner, Zeits. f. Kryst. **39**. 155. (1904).

4) B. Gossner, Zeits. f. Kryst. **38**. 110, 159, 161. (1904).

5) P. Fischer, Dissertation Göttingen, (1911), p. 10, 25.

that in reality in the case of the *ammonium-salt* a discontinuous change may be present between 124° and 135° C., so that a polymorphic change seems to follow immediately the first one.

From this it appears that the phenomenon of *polysymmetry* must be distinguished from the case of true *polymorphism*<sup>1)</sup>; and for the explanation of the latter, Mallard's theory cannot therefore serve. It must however be remarked that pseudosymmetrical substances can often be changed at higher temperature into new, true polymorphic modifications<sup>2)</sup>: *potassium-sulphate* is a well-known example of this, it being suddenly changed at about 650° C. into a new, really hexagonal modification.

Also combinations of polysymmetrical and real polymorphic changes may occur with the same substance<sup>3)</sup>.

Cases of this are: *propylamine-stanni-chloride*<sup>4)</sup>:  $(C_3H_7 \cdot NH_2)_2SnCl_6$ ; *diethylamine-platini-chloride*:  $[(C_2H_5)_2NH]_2PtCl_6$ ; *diethylamine-stanni-chloride*:  $[(C_2H_5)_2NH]_2SnCl_6$ , which even in its external habit completely simulates a cubic crystal; *tripropylamine-platini-chloride*:  $[(C_3H_7)_3NH]_2PtCl_6$ ; *tetra-ethyl-ammonium-stanni-chloride*:  $[N(C_2H_5)_4]_2SnCl_6$ , where the lamellar structure of the monoclinic, but pseudocubic crystals is very distinctly recognisable; *tetrapropylammonium-platini-chloride*:  $[(C_3H_7)_4N]_2PtCl_6$ ; and *tetramethylammonium-platini-chloride*:  $[N(CH_3)_4]_2PtCl_6$ , where however a rather similar case perhaps occurs to that of the *isopropylamine-platini-chloride* previously mentioned. While in the case of real polymorphism, metastable states may occasionally occur under the influence of retardative circumstances, it must be clear from what has been said about polysymmetrical changes in general, that no such metastable conditions can be here in question.

§ 12. From these and many other researches it has gradually become clear that even if a crystal be apparently a homogeneous individual, only in rare cases it may be considered as a really homogeneous thing. According to Mallard's views and those of a number of other investigators, the molecular arrangements which are charac-

1) J. Beckenkamp, Zeits. f. Kryst. **34**. 633. (1901). The author suggests to adopt Mallard's theory in all cases of so-called polymorphism, where both modifications have the same or only unappreciably different specific gravities.

2) P. Groth, Einleitung in die Chemische Krystallographie (1904), p. 6.

3) P. Groth, loco cit. p. 7.

4) A. Ries, Zeits. f. Kryst. **39**. 50, 55, 56, 66, 69, 73. (1904); **36**. 360. (1902); **49**. 513. (1911).

teristic of crystalline matter, do *not* necessarily possess the perfect homogeneity involved by Hessel's and Bravais' theories<sup>1)</sup>. Its constituting and identical molecules are therefore not always parallel to each other, but they may have different orientations in space, depending on the special symmetry of the crystalline substance. In very numerous cases it is built up from lower symmetrical masses according to the general laws of twin-formation.

The fact that it is just those space-lattices whose dimensions are such as to make them appear to possess an *approximate* symmetry, which show most conclusively, that tendency to aggregate into apparently higher symmetrical complexes whose twinning-elements correspond with the approximate symmetry-elements of these simulated higher symmetrical complexes, was certainly first recognised in its general significance by Mallard. But from this to his later views, that *all* space-lattices should really be *pseudo-cubic*<sup>2)</sup>, or that *all* higher symmetrical crystals should only be pseudo-symmetrical aggregations of submicroscopical lamellae of lower symmetry, — is a long way. A rational proof of these views cannot at present be given, and as such these hypotheses have no immediate value for our knowledge in its present state. But even if we leave these views aside, it can only be once more emphasised, that the idea of lamellar aggregation has been, and in future will prove, a very successful one in the explanation of a great number of the most interesting phenomena in the science of inorganic matter.

§ 13. In this and the preceding chapters we were able to compare on several occasions the specific symmetry of objects in inanimate and in living nature. As strikingly different features of the symmetry-properties revealed in both domains we must chiefly bear in mind two important facts: 1) the occurrence in living nature of symmetry-axes which are characterised by *irrational* values of the cosines of their periods  $\alpha$ ; and 2) the much higher symmetry of the

<sup>1)</sup> J. Beckenkamp, *Statische und Kinetische Krystalltheorien I*, p. 194. (1913).

<sup>2)</sup> E. Mallard, *Bull. de la Soc. Minér.* 7. 349. (1884); 9. 54, 123. (1886). F. Wallérand, *ibidem*, 24. 159. (1901).

This theory however has in recent times got a new support, although in somewhat modified form, by the dynamical views of J. Stark. According to this investigator, *rock-salt* for instance would be built up by three submicroscopical systems of tetragonal-hemimorphic symmetry. They form a quasi-homogeneous complex of apparently holohedral cubic symmetry. Similar ideas are found in a paper of Beckenkamp (Cf.: J. Stark, *Jahrbuch f. Radioaktiv. und Elektronik.* 12. 280. (1915).

*older* species of animals, in comparison with that of the living beings of later periods of evolution. Indeed, after what we have seen in the last chapter, in non-living nature there seems to be rather an oppositely directed tendency, a drift towards the highest degree of symmetry possible. The cases of apparent and mimetic symmetry dealt with in the above may serve to sustain this view; further the fact that polymorphic substances generally change into higher symmetrical forms, when temperature increases. In the next chapter we shall obtain yet more evidence for this view: we shall see, that optical antipodes, possessing only symmetry-properties of the first order, have a natural tendency to pass into optical *inactive* systems exhibiting symmetry-properties of the second order also. A certain tendency to form the more symmetrically built molecules in cases, where several isomerides may occur simultaneously, is observed on many occasions by chemists also, and it is a well-known fact for instance, how easily the threefold symmetrically substituted derivatives of *phenoles*, *aniline*, etc. are commonly produced, in comparison with their less symmetrical isomerides.

On the contrary, evolution in living nature seems to proceed in exactly the opposite direction, the lower animals showing in many cases a much higher symmetry than the mere bilateral one of the animals, which have appeared in the later periods of the earth's history. A certain preference for pentagonal symmetry, both in the case of animals and of plants, seems to exist even here, — a symmetry so closely related to the important ratio of the "golden section," and unknown in the world of inanimate matter.

The view, that really the *older* forms should possess the *higher* symmetries, is probably also sustained by the remarkable phenomena of the occurrence of so-called *peloria*<sup>1)</sup> in flowers.

It has been observed for a long time that many plants, the flowers of which have only bilateral symmetry, suddenly produce at the top of an inflorescence a flower which shows the perfect symmetry of one of the axial groups, or of the groups  $C_n^V$ . Thus *Delphinium peregrinum* produces occasionally a completely pentagonal blossom; the common *fox-glove* (*Digitalis purpurea monstrosa*) exhibits the same phenomenon (fig. 156), as the accompanying figure (after H. De Vries) clearly shows. Among *Orchidaceae* the species *Cattleya marginata* and *Phalaenopsis Schilleriana* occasionally show a *pelo-*

1) From:  $\pi\acute{\epsilon}\lambda\omega\rho = \text{monstrum}$ .

rium of perfect ternary symmetry. <sup>1)</sup> This remarkable phenomenon is commonly observed in the flower which stands at the apex of a



Fig. 156.  
Pelorium of *Digitalis*  
*purpurea monstrosa*.

stem or in the centre of an inflorescence, and the changed flower has moreover a tendency to take a more upright direction of growth than is usual for it. (*Antirrhinum maius*; *Digitalis*; etc.). When such an irregular blossom becomes symmetrical, this may occur in two different ways: either the development of such parts which determine the lack of symmetry in the ordinary individuals, is stopped, or the irregular parts are produced in greater number, so that a higher symmetrical complex is the final result. In the first case it is said that a "regular pelorium" is produced, in the latter case the "irregular" one.

The regular pelorium is therefore a product of *stagnation* in the natural development of the blossom, the irregular pelorium is the result of an *excessive development* of certain parts of it.

At present the phenomenon is generally explained in both cases as a *retrogression* towards an older prototype. According to this view, the occurrence of peloria is a case of atavism, of typical retrograde mutation. The irregular or less symmetrical flower is the descendant of a higher symmetrical ancestor; and also here the *older form* therefore appears to be that of *higher* symmetry.

Indeed, it can hardly be denied that there is a sharp line of demarcation between the forms of inanimate and living nature with respect to the part the principle of symmetry takes therein: here the gradual evolution of forms from higher towards lower symmetry, and the characteristic preference for the irrational ratio of the "aurea sectio"; there the tendency towards higher symmetry as to a condition of greater mechanical stability, and the exclusion of all irrational ratios in the periods of the symmetry-axes. There is no way to escape the urgency of this conclusion, and only the question may arise: can we hope that further investigation shall enable us in future to overcome this barrier?

In the author's opinion the contrast may be such of an only *apparent* nature, in so far, as the products of living nature do *not* possess the character of absolute mechanical stability. The restless process of growth and metabolism in living nature, the never stopped current of consecutive events in the chain of life-evolution, is rather based upon *a certain lack of mechanical stability* of the stages successively arrived at. Highest mechanical stability corresponds however only to highest possible symmetry under existing conditions; and only because in living nature no such perfect mechanical stability can be reached, the direction of natural events seems to be contradictory to this principle. We shall return to these questions afterwards.

## CHAPTER VIII.

### PASTEUR'S LAW.

Pasteur's Discovery of the Fission of Racemic Acid. — Molecular Dissymetry and Optical Activity. — Fission-Methods. — Spontaneous Crystallisation; Problems and Investigations. — Transition-temperature. — Partial Racemism. — Physiological action of Optical Antipodes. — Enzyme-Action. — Pseudo-Racemism. — Racemisation, its Mechanism and Equilibrium. — Pasteur's General Conclusions. — The Theory of the Asymmetric Atom. — Pasteur's Law and Van 't Hoff-Le Bel's Theory; Problems and Investigations. — The Symmetry of Chemical Molecules. — Crystallonomical Relations; Problems and Data. — Chemical Composition and Optical Rotatory Power. — Asymmetric Metal-atoms. — Enantiomorphism of Cyclic Compounds. — Enantiomorphous Configuration and Hemihedrisism. — Final Remarks.

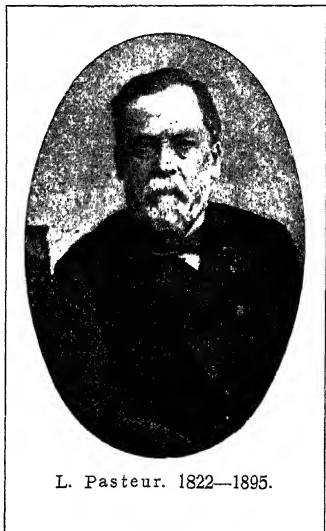
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.... "Our knowledge of that aristocracy of chemical compounds which possess, in addition to all the commonplace and vulgar physical attributes, the distinctive seal of nobleness: optical activity."

Percy Frankland, 1891.

§ 1. It was in 1848 that Pasteur, at the very beginning of his scientific career, made his famous discovery that when the sodium-ammonium-salt of racemic acid:  $C_4O_8H_8$ , was recrystallised from an aqueous solution at lower temperatures, it deposited two kinds of crystals which were non-superposable mirror-images of each other. The organic acids set free from both kinds of crystals after careful selection, appeared to have the same composition as the racemic acid itself. But the one, if dissolved in water, made the plane of a linear polarised beam of light passing through its solution deviate through a certain

angle in one direction, while the other acid under analogous circumstances made it deviate through the same angle, but in just the opposite direction. The dextrogyratory acid was proved to be identical with the ordinary, already well-known, *tartaric acid*; the laevogyratory acid appeared to be another, isomeric, *tartaric acid*, unknown up to that date. Not only both acids themselves, but also the various salts derived from them, appeared in each case to have enantiomorphous crystal-forms, while their chemical behaviour evidently was always identical. However the solutions of the left-handed crystals made the plane of polarisation of a traversing polarised light-beam constantly rotate in just the opposite direction, to that which solutions, prepared from the right-handed crystals, did.<sup>1)</sup>



L. Pasteur. 1822—1895.

Seldom has a scientific discovery had such far reaching consequences, as this one had. The connection between the non-superposable mirror-images of the crystal-forms of the isomeric substances and the oppositely directed rotatory power of their molecules, seemed proved beyond all doubt.

Neither could there be any doubt as to the structural identity of the two *tartaric acids*, and the explanation given by Pasteur himself<sup>2)</sup>: that the special arrangement of the atoms in the molecules of both acids must necessarily be supposed to be related to each other, as that of two "non-superposable" stereometrical figures, led not only to the conception of a new kind of isomerism, but it marked the very starting-point of our views concerning the special arrangement of the atoms of chemical molecules in general; and a quarter of a century later it opened the way to that new branch

1) L. Pasteur, *Ann. de Chim. et Phys.* (3). **24**. 442. (1848); *Compt. rend. de l'Acad. d. Sciences Paris*, **26**. 535; **27**. 367 101. (1848).

2) L. Pasteur, *loc. cit.*



of chemical science which now is commonly indicated by the name of *stereochemistry*<sup>1)</sup>.

Pasteur<sup>2)</sup>, as a consequence of his work on this "molecular dissymmetry", soon put the question to himself: are the atoms of the righthanded compound to be considered as grouped on the spirals of a dextrogyratory helix, or as placed at the summits of an irregular tetrahedron? Both views involve arrangements which are non-superposable with their mirror-images. However the last step necessary to lead to the general conception of the "plurivalent asymmetric atoms", was not made by him. It was Van 't Hoff<sup>3)</sup> and Le Bel<sup>4)</sup>, who in 1874 simultaneously and independently of each other formulated the important generalisation of the asymmetric carbon-atom, at once making it possible to extend over the whole domain of organic chemistry Pasteur's fundamental views on the special configuration of the atoms. As we shall see, Pasteur's statement of the case is, however, more general than that of the theory of Van 't Hoff and Le Bel.

It is to Pasteur's genius moreover, that we are indebted for the general methods now in use for the fission of racemoids into their optically active components<sup>5)</sup>. They were the result of his splendid and continual investigations during more than a full decade. Before we go further into the conclusions of general significance, to which the various facts gathered in this way have gradually led, it seems better to deal more in detail with these various methods of fission, and to consider at the same time the most important

<sup>1)</sup> The innumerable investigations on the rotatory power of organic molecules, its dependence on concentration, temperature, wave-length, chemical constitution, etc. are not considered in detail in this chapter, although some data are occasionally given for the purpose of illustrating other facts. For a full treatment of these phenomena the author must refer the reader to the original papers of Th. S. Patterson, P. Frankland, Ph. A. Guye, P. Walden, H. Rupe, and many others; the results are dealt with e. g. in: H. Landolt's "Das Drehungsvermögen organischer Verbindungen", in C. A. Bischoff und P. Walden's: "Handbuch der Stereochemie", in A. Werner's "Lehrbuch der Stereochemie" etc., and in many fuller or more restricted textbooks on stereochemistry.

<sup>2)</sup> L. Pasteur, Deux Leçons sur la Dissymétrie Moléculaire, professées devant la Société Chimique de Paris, (1860).

<sup>3)</sup> J. H. van 't Hoff. Voorstel tot Uitbreiding der tegenwoordig in de Scheikunde gebruikte Structuurformulés in de Ruimte, (1874).

<sup>4)</sup> J. A. Le Bel, Bull. de la Soc. Chim. de Paris, (2). 22. 337. (1874).

<sup>5)</sup> L. Pasteur. Compt. rend. 36. 191. (1852); 51. 298. (1860); Ann. de Chim. et Phys. (3). 38. 437. (1853); Deux Leçons etc. loco cit.

facts relating to them, which have been detected since that period.

§ 2. I. *Spontaneous Fission of Racemic Compounds into their Components by mere Crystallisation from Solutions.*

The phenomenon first discovered by Pasteur, that a racemoid by simple recrystallisation from a solution deposits the crystals of both its optically active components separately, has since been observed in a restricted number of cases. It appeared however for a considerable time to be quite fortuitous, whether the desired fission of the racemic compound occurred in this way, because the special circumstances under which it takes place seemed to be completely unknowable. Pasteur himself, who clung persistently to the idea that molecular dissymetry could only be produced by the action of living organisms, assumed that the fission by spontaneous crystallisation was started by micro-organisms introduced from the atmosphere. Since then it has been found that the phenomenon takes place in cases where the inactive mixture of the components is at the same temperature less soluble than the racemic compound. This signifies, that the racemic compound is the less stable, or "metastable" solid phase with respect to the saturated, optically inactive solution, in comparison with the crystalline mixture of the active components with respect to it. As however these relations are a function of the temperature, it is necessary to consider this case more in detail.

The classical example of a fission of this kind is that of Scacchi's sodium-ammonium-racemate <sup>1)</sup>:  $C_4H_4O_6(NH_4)Na + H_2O$ . If this salt be recrystallised from aqueous solutions at temperatures below  $27^\circ C$ , it is deposited as a mixture of right-, and left-handed crystals of the corresponding optically active *tartrates* ( $+ 4H_2O$ ), having the axial symmetry  $D_2$ .

It was afterwards demonstrated by Van 't Hoff <sup>2)</sup>, that this case of spontaneous fission is completely analogous to that of the formation and decomposition of many double-salts, there being

1) A. Scacchi, Rendic. dell' Acad. di Napoli (1865). 250; cf. W. Städel, Ber. d.d. Chem. Ges. 11. 1752. (1878); G. Wyruboff, Compt. rend. de l'Acad. d. Sc. Paris 102. 627. (1886); Bull. de la Soc. Chim. (2) 41. 210. (1884); 45. 52. (1886).

2) J. H. van 't Hoff and C. Van Deventer, Zeits. f. phys. Chemie 1. 173. (1887); J. H. van 't Hoff; H. Goldschmidt, and W. P. Jorissen, Zeits. f. phys. Chemie 17. 49, 505. (1895); J. H. van 't Hoff, Vorlesungen ü. theor. u. phys. Chemie, II. (1899), p. 100; idem, Vorlesungen ü. Spaltung und Bildung von Doppelsalzen, (1897), p. 81; W. Meyerhoffer, Gleichgewichte der Stereoisomeren, Leipzig, (1906).

a definite *transition-temperature*, above which the racemic compound is stable, while on the contrary at a temperature below it, the equimolecular mixture of both *tartrates* is the more stable solid phase in equilibrium with the optically inactive, saturated solution.

It was found that an equimolecular mixture of the dextro-, and laevogyrotary *tartrates* at  $27^{\circ},2$  C. was transformed into Scacchi's racemate, while three quarters of the water of crystallisation was set free. This racemate however appears only to exist between  $27^{\circ},2$  C. and  $36^{\circ}$  C., because above  $36^{\circ}$  C. it is changed into a mixture of *sodium-racemate* and *ammonium-racemate*; both these salts could be obtained from a solution at  $40^{\circ}$  C. The transition-temperature of a mixture of the right-, and lefthanded salts into the two mentioned racemates, lies at about  $29^{\circ},2$  C.

In this case the transition-temperature was a *minimum* temperature for the sphere of existence of the racemate; however this need not be the case always. Thus, while e. g. *potassium-sodium-racemate* ( $+ 3H_2O$ ), with its transition-temperature of  $-6^{\circ}$  C., is quite analogous to Scacchi's racemate in this respect <sup>1)</sup>, the *rubidium-racemate* ( $+ 2H_2O$ ) was found <sup>2)</sup> to have a transition-temperature of  $40^{\circ},4$  C., this however being for it a *maximum* temperature; so that at temperatures *above*  $40^{\circ},4$  C. the spontaneous fission into the optically active components occurs, while all the water of crystallisation is set free. Evidently the occurrence of such a minimum or maximum transition-temperature for a racemate, is intimately connected with the algebraic sign of the heat-effect accompanying its formation, — a fact completely in agreement with the law of mobile equilibrium. In the cases mentioned, the heat-effect is of course related also to the setting free of, or to the combination with, some molecules of water of crystallisation; but also when this complication does not occur, the explanation as given here, must hold.

Thus from an optically inactive solution of the right-and lefthanded *methylmannosides* (mpt:  $193^{\circ}$  C.), either a mixture of the two active forms, *or* the racemic compound (mpt:  $193^{\circ}$  C) may be obtained, according to the crystals being deposited below  $8^{\circ}$  C. or above  $15^{\circ}$  C. <sup>3)</sup>. The transition-temperature for the racemate (*minimum*)

<sup>1)</sup> J. H. Van 't Hoff, loco cit.

<sup>2)</sup> J. H. Van 't Hoff, Vorlesungen ü. theor. und phys. Chemie, II. (1899), p. 104; J. H. Van 't Hoff and W. Müller, Ber. d. d. Chem. Ges. **31**. 2206. (1898).

<sup>3)</sup> E. Fischer and L. Beensch, Ber. d. d. Chem. Ges. **29**. 2927. (1896).



The isotherms  $Oa'$  and  $Ob'$  are in the same way solubility-curves for another temperature  $t'$  situated *below* (fig. 157) or *above* (fig. 157) the transition-temperature under atmospheric pressure. At  $Q$  and  $P$  they will meet the solubility-isotherm  $PrQ$  for the racemate, the solubility of which is of course influenced by an excess of the right- or left-handed component.

The point  $r$  is the optically inactive solution which is saturated with respect to the racemoid, the point of intersection  $x$  represents the more concentrated, metastable, inactive solution which would be in

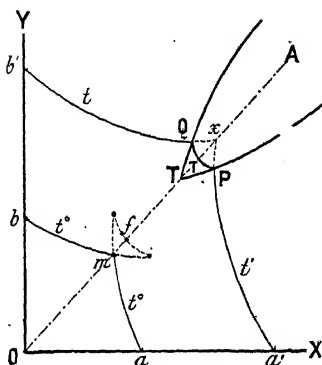


Fig. 158.

equilibrium with a *mixture* of the components at the same temperature, if this equilibrium could be realised. This metastable solution would be super-saturated with respect to the racemic substance.

At the transition-temperature itself, the solution  $T$  may exist in stable equilibrium with the racemic compound, or with the right- and lefthanded components. Thus on  $TQ$  are all solutions which, at increasing (or decreasing) temperatures, are

simultaneously saturated with respect to the racemate + excess of the left component, and on  $PT$  are just all solutions which behave in the same way with respect to the racemate + excess of the right component. If, perpendicular to the plane of the figure, a third axis  $OZ$  be taken as temperature-axis, a complete survey of these relations can be given in a tridimensional model.

The whole behaviour is completely analogous to that of ordinary double-salts<sup>1)</sup>, the only difference here being this, that the whole figure is *fully symmetrical* with respect to the line  $OA$  bisecting the angle between the axes  $OX$  and  $OY$ , in consequence of the identical chemical and scalar physical properties of both optically active components.

As to the question whether racemic compounds be really present in the liquid state, it may be briefly remarked here that there is

<sup>1)</sup> H. W. Bahhuis Roozeboom; *Zeits. f. phys. Chemie* 2. 513. (1888); 10. 145. (1892); F. A. H. Schreinemakers, *ibidem* 9. 57. (1892).

little probability of it. According to Kruyt and Van der Linden <sup>1)</sup>, they seem to occur only to an unappreciable amount in the cases studied up till now, if present in the liquid state at all.

Shibata <sup>2)</sup> proved moreover that the absorption of light of the *racemic* complex *cobalti*-salts in aqueous solutions, and that of their optical antipodes under the same conditions, is completely *the same*. This fact seems also to indicate that *no* such racemic compounds really exist in solutions to any appreciable degree.

We have seen that as long as the racemoid is stable, the concentration of the metastable solution *x* which possibly is in temporary equilibrium with a *mixture* of both components, will be *greater* than that of the stable solution in equilibrium with the racemic compound at the same temperature. As a complement of this it may be remarked that the reverse must be the case if the racemoid is *no* longer the stabler solid phase, as is easily seen from the figures 157 and 158, when the inactive solution *m* is compared with *f*, which is a metastable optically inactive solution, eventually in equilibrium with the racemic substance at the same temperature. Here also therefore the less stable phase has always the greater solubility, as is observed in all such cases.

Of course it would have also been possible to deduce all these relations from sections through the tridimensional model parallel to the coordinate-planes *XOT* or *YOT* respectively, i. e. by means of temperature-concentration-diagrams. This is the method principally followed by Van 't Hoff, in his work on the formation and decomposition of double-salts <sup>3)</sup>.

§ 4. The solution of the problem why a number of racemoids can be spontaneously resolved by crystallisation and separating both kinds of enantiomorphous crystals from each other by selection, while others cannot be separated in this way, — must evidently depend on the situation of the transition-temperature. If this lies in the neighbourhood of the temperature of crystallisation and within the range of temperatures where the substances can exist without decomposition, there will be great probability that the spontaneous fission mentioned above, really occurs, be it at higher

1) T. Van der Linden, Ber. d. d. Chem. Ges. **44**. 963. (1911); H. R. Kruyt, *ibid.* **44**. 995. (1911); A. Ladenburg, *ibid.* **44**. 1677. (1911).

2) Y. Shibata, Journal of the College of Science Imp. Univ. Tokyo, **37**. Art. 2. p. 28. (1915).

3) J. H. Van 't Hoff, Vorlesungen ü. Bildung und Spaltung von Doppelsalzen, *loco cit.*

or at lower temperatures, and provided that supersaturation be avoided in the case of lower temperatures. But if the transition-temperature be too far removed from the ordinary temperatures of crystallisation, in most cases it will be by no means possible to resolve the racemoid into its components in the way described, and then it becomes necessary to look for other methods of fission. Cases of this kind are the most numerous: thus, e. g., that of *racemic acid* itself, and the dextro-, and laevogyrotary *tartaric acids*, in contradiction to the cases of their *salts* above dealt with. A similar case is that, where *no racemic compound* could be obtained, although both the optically active components be well-defined crystallised substances. Such cases are for instance: *d*-, and *l*-*asparagine*:<sup>1)</sup>  $\text{CO}(\text{NH}_2)\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH} + \text{H}_2\text{O}$ , and the *d*-, and *l*-*gulonic lactones*<sup>2)</sup> (mpt:  $181^\circ \text{C}$ .):  $\text{C}_6\text{H}_{10}\text{O}_6$ , which all have the symmetry of the group  $D_2$ , but whose racemoids have not so far been obtained. Here also the temperature at which the inactive mixture is changed into the racemic compound, when in contact with its solution, must be supposed to lie too far removed, to allow its formation from the components.

§ 5. Fairly soon however it appeared that the transformation of the racemic compound into its active components could happen also under circumstances in which the racemic compound itself must be considered as undeniably stable.

Gernez<sup>3)</sup> first drew attention to the fact that from an optically inactive solution of two active components, *if supersaturated*, the excess of the solute was precipitated wholly as *one* of the active components, if a small crystal of that component or of an isomorphous or isodimorphous substance, was added to the supersaturated solution as a nucleus of crystallisation. The same was demonstrated afterwards by Purdie<sup>4)</sup> in the case of *zinc-ammonium-lactate*, while in 1898 analogous experience was obtained to a certain extent by Kipping and Pope<sup>5)</sup>, namely in so far that on recrystallising *sodium-ammonium-racemate* from solutions in the open air and in

<sup>1)</sup> A. Piutti, Rend. Acad. d. Sc. Napoli (3). **10**. 69. (1904); Gazz. Chim. It. **34**. II. 36. (1904).

<sup>2)</sup> E. Fischer and R. S. Curtiss, Ber. d. d. Chem. Ges. **25**. 1025. (1892).

<sup>3)</sup> D. Gernez, Compt. rend. de l'Acad. d. Sc. Paris, **63**. 843. (1866); Jahresber. (1866), p. 400.

<sup>4)</sup> T. Purdie, Journ. Chem. Soc. London **63**. 1143. (1893).

<sup>5)</sup> F. S. Kipping and W. J. Pope, Journ. Chem. Soc. London, **95**. 103. (1909).

exsiccators, a preferential deposition of a little of the dextrogyratory salt was several times observed, probably under the influence of optically active nuclei in the laboratory-dust.

A systematic study of some of these phenomena was made by Ostromisslensky<sup>1)</sup>, but especially in cases where the racemic compound is *not* the stable one in comparison with the mixture of the components. He observed, that an inactive solution of right- and left-handed *sodium-ammonium-tartrates*, if *supersaturated*, and inoculated at 6° C. by a nucleus of *laevogyratory asparagine*, will deposit exclusively the *dextrogyratory tartrate*. Because Gernez had already demonstrated that a supersaturated solution of the *dextrogyratory tartrate* is *not* started to crystallisation by inoculation with a crystal of the *left* salt, Ostromisslensky concludes from this experiment that the *laevogyratory asparagine* is structurally more closely related to the righthanded *sodium-ammonium-tartrate*, than even the lefthanded *tartrate* itself.

In the same way a preferential crystallisation of the dextrogyratory component was observed, if in this case as a nucleus of crystallisation small quantities of *potassium-tartrate*, *sodium-tartrate*, and *ammonium-malate* were used; the direction of the rotary power of the salt deposited, appeared in all cases to be *the same* as that of the introduced nucleus. Even the *monoclinic ammonium-tartrate*, which however, according to Pasteur<sup>2)</sup>, may occasionally occur in a rhombic form also, — had the same effect; therefore it seems reasonable to suppose that *isodimorphous* substances also can produce the same effect. Most remarkable is the fact that substances *which have no rotatory power at all*, may also be used as crystallisation-nuclei, and with the best results, if only the inoculated crystal show a "non-superposable" hemihedrism.

Thus from an inactive solution of *asparagine*, by the introduction of a crystal of *glycocoll*:  $\text{CH}_2(\text{NH}_2)\text{COOH}$ , the one component was deposited principally, although not in all experiments however. Here again is a wide field open for investigation. If we adopt the view of Ostromisslensky that the crystals of *glycocoll* are really hemihedral, these experiments seem to prove indisputably, that the enantiomorphous nucleus exercises an exclusive, directional force, perhaps in the same way as in the experiments

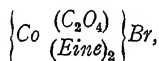
1) I. Ostromisslensky, Ber. d. d. Chem. Ges. **41**. 3035. (1908); Journ. russ. phys. chem. Ges. **42**. 102, 606. (1910).

2) L. Pasteur. Jahresber. (1854), p. 395.

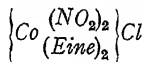


of Kipping and Pope <sup>1)</sup>, in which a preferential deposition of the one or the other component was obtained, when solutions of the *sodium-ammonium-tartrates*, or of *sodium-chlorate*, nearly saturated with *dextrose* or with *levulose*, slowly crystallised. In all these cases the experiments were made within a range of temperatures, where the racemic compound was certainly no longer the stabler solid phase <sup>2)</sup>. Ostromisslensky now suggests that this condition must always be fulfilled, and even to such an extent that in the occurrence of the phenomenon described, he sees a new criterion for discriminating between true racemic compounds and inactive, externally compensated, mixtures in general.

On the other hand, experiments recently made by Werner <sup>3)</sup> on the spontaneous fission of inorganic molecules, seem apparently to prove the possibility of such a separation, even under circumstances where racemic compounds are supposed to be really stable. This investigator found, that if the active components are only less soluble than the racemic substance, the optically inactive, supersaturated aqueous solution may be precipitated by the addition of alcohol, or of a mixture of alcohol and ether, under preferential deposition of one of the two components, if only a slight excess of that active component, or of an active substance isomorphous with it, be first added to the solution. In such a way it appeared, for instance, possible to separate the *racemic oxalo-diethylenediamine-cobalti-bromide*:



and the *racemic dinitro-diethylenediamine-cobalti-chloride*:



into their strongly active components. <sup>4)</sup> It appears also possible to separate the last mentioned racemoid, by precipitation with alcohol, after the addition of about 10% of the corresponding active *oxalo*-compound.

1) F. S. Kipping and W. J. Pope, Proc. Chem. Soc. **14**. 113. (1898); Journ. Chem. Soc. London **73**. 606. (1898); Zeits. f. Kryst. **30**. 472. (1899); Chem. News **75**. 46. (1897); Cf. also: Ch. Soret, Archiv. des Sc. phys. et nat. de Genève (4). **7**. 80. (1899).

2) Of course the case of *sodium-chlorate* is not considered now.

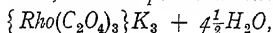
3) A. Werner, Ber. d. d. Chem. Ges. **47**. 1955, 2171, 2179. (1914).

4) Here and in the following, *Eine* is again used as an abbreviation for *ethylene-diamine*:  $\text{C}_2\text{H}_4(\text{NH}_2)_2$ .

The analogous *oxalo-diethylenediamine-chromi*-salt, of which up till now the fission into its active components could not be performed in any other way, was readily separated by the addition of 10% of the *dextrogyrate oxalo-cobalti*-salt, and precipitation with alcohol; in this way the righthanded isomeride was obtained, while from the mother-liquid the laevogyrotory salt could easily be isolated. This method of fission is undoubtedly closely related to that of Ostromisslensky and Gernez, as by the rapid cooling of the solutions previously saturated at somewhat higher temperatures, supersaturation will also be produced in this case to a greater or smaller degree.

But it may appear doubtful whether the assumption of „stable” racemoids under these circumstances may be considered justified at all, where the author himself emphasizes that the antipodes must be „less soluble” than the racemic compound: this, in fact, seems to exclude any other view than that the racemoid is really the *less stable* solid phase with respect to the saturated solutions.

According to Werner, *racemic potassium-rhodium-oxalate*:



would be separated into both its active components by spontaneous crystallisation if a solution of the salt saturated at its boiling point, and after being rapidly brought to 90° C, is slowly cooled until room-temperature is reached. Two kinds of crystals which would be enantiomorphously related, would be deposited from the solution. After selection under the microscope, a crystal of each kind, if it simply remained in the saturated mother-liquid at room-temperature for a long time, would slowly grow to rather large individuals.

However these statements must, in the present writer's opinion, be considered erroneous. For the solubility of the active components is appreciably *greater* at room-temperature than that of the racemic salt, the latter being therefore the stabler phase under the prevailing conditions. Indeed, it was shown by direct experiments <sup>1)</sup>, that a crystal of the active components, if brought into the saturated or slightly supersaturated solution of the racemic compound, will rapidly disintegrate and afterwards disappear completely. From the solution, however, only the *trichinic* crystals of the racemic compound can be obtained, which by their *accidental* development can eventually make the impression of being non-superposable with their mirror-images. Obviously the crystal-forms reproduced

<sup>1)</sup> F. M. Jaeger, Proceed. Kon. Acad. v. Wet. Amsterdam, **19**, June, (1917).

in Werner's figures are merely distorted *triclinic* crystals of the racemic salt. From a theoretical point of view it would, moreover, be quite incomprehensible that the more soluble crystals of the optically active components should grow in a solution of the less soluble racemic compound, under conditions where the latter is obviously perfectly stable.

The possibility of a spontaneous fission of this salt can therefore not be considered as proved by Werner's experiments, and still remains an open question <sup>1)</sup>.

§ 6. As a result of all the investigations hitherto made on the subject, we may say that the fact of the spontaneous fission of racemoids into crystals of the optically active components, if recrystallised from a suitable solvent, has been in many respects elucidated, especially with respect to the part which the transition-temperature has therein. But the behaviour of the supersaturated solutions in contact with a nucleus of crystallisation, whether it be of a crystal of one of the optically active components themselves or of an isomorphous or isodimorphous substance, appears a rather puzzling problem yet in many points. A solution supersaturated with respect to the racemate, is within the sphere of existence of the racemate, à fortiori and appreciably *more* supersaturated with respect to the mixture of the components. This may appear a fact which makes it seem natural that a nucleus of one of the components, if introduced into the supersaturated solution under these circumstances, will provoke crystallisation; and something of an analogous character may be imagined to take place in the case of the alcoholic precipitation from aqueous solutions, as in Werner's experiments. But then it remains entirely enigmatic still, why in such cases *exclusively* the *one* component is deposited: the way in which this directional influence of the nucleus introduced acts on the supersaturated solution, still remains wholly outside the scope of mechanical explanation.

More, and rigorously systematical, observations and experiments must be made, before the required insight into this problem can be obtained.

§ 7. II. *Fission of Racemoids by Combination with optically active Substances.*

As a rule the method of fission dealt with in the preceding paragraphs, does not lead to the desired result, because for some reason

<sup>1)</sup> F. M. Jaeger, *Chemisch Weekblad*, Vol. 14, pag. 726. (1917).

or other, circumstances appear not favorable for spontaneous fission. In such cases a second, and from a practical standpoint, the most important method of separation, — also found by Pasteur, — is made use of. It is by this method that most substances which may occur in two non-superposable mirror-images, have up till now, been resolved into their components.

The principle on which this method is founded, is, that when two stereometrical arrangements which are non-superposable mirror-images  $A$  and  $A'$  of each other, are combined in a corresponding way with another stereometrical complex  $f$ , also being different from its mirror-image  $f'$ , the two figures  $Af$  and  $A'f$  thus produced *will no longer be mirror-images of each other*.

The truth of this can be easily demonstrated; for if  $Af$  be reflected in a mirror, it is changed into its mirror-image  $A'f'$ . This figure  $A'f'$  however is certainly different from  $A'f$ , because  $f$  and  $f'$  are *non-superposable* mirror-images of each other. Therefore  $Af$  and  $A'f$  can *never* be mirror-images of each other, unless  $f$  and  $f'$  be congruent, which however is *not* the case in this method of operation.

If instead of  $f$ , we had used its mirror-image  $f'$ , we should have obtained the complexes  $Af'$  and  $A'f'$ ; of course these will not be each other's mirror-images either. But  $A'f'$  and  $Af$ , and in the same way  $A'f$  and  $Af'$ , are truly two pairs of such mirror-images. As we shall see, this last fact can be made use of for obtaining *both* antipodes of a racemoid by the same method of fission.

All right and left-handed isomerides have identical *scalar* properties, and also the same chemical constants. Thus they have the same solubility in the same solvent, identical melting-, and boiling-points, the same affinity-constants in their reactions with optically inactive substances, the same densities, etc. Substances which are not related as mirror-images, have however different solubilities under similar circumstances. It will therefore be possible to separate them by *fractional crystallisation*; thus e. g.  $Af$  and  $A'f$ , or  $Af'$  and  $A'f'$  would be symbols for compounds which could be separated in this way. Because only the less soluble compound can be obtained *perfectly pure* in this way, while the other one always has some of the less soluble substance adhering to it, the *pure* salts  $Af$  and  $A'f'$  can, properly speaking, only be obtained by successive combination <sup>1)</sup> of the racemoid  $AA'$  with  $f$  or  $f'$ . However in practice the difference

<sup>1)</sup> W. Marckwald, Ber. d. d. Chem. Ges. 29. 43. (1896).

of solubility is often sufficiently great to allow a practically complete fission of  $AA'$  by simply combining it with  $f$ .

If, however, the difference of the solubilities between  $Af$  and  $A'f$  is not great enough, a useful modification of the method described was proposed by Pope and Peachy<sup>1)</sup>. If only so little of  $f$  be present, as to give precisely the theoretical quantity of the less soluble compound  $Af$ , while the other component  $A'$  of the racemoid be bound to some optically inactive substance  $p$ , giving with it a very soluble compound  $A'p$ , then, — if the solution is allowed to crystallise slowly, a certain amount of  $Af$  will every moment be withdrawn from the equilibrium-mixture in the remaining solution. As a consequence, this equilibrium will be displaced so that a new quantity of  $Af$  is produced, which again will be deposited; etc.

The result is that  $Af$  is completely gained in the crystalline state, while  $A'p$  remains in the mother-liquid, from which  $A'$  can easily be isolated afterwards. Pope and Peachy have used this method e. g. to separate the *racemic tetrahydro-quinaldine* into its optically active components, by means of the action of *ammonium-bromo-camphor-sulphonate* (1 mol.) on inactive *tetrahydro-quinaldine-hydrochloride* (2 mol.); etc.

If the combinations  $Af$  and  $A'f'$  are sufficiently loose, it will afterwards be possible to set  $A$  and  $A'$  free by fixing  $f$  and  $f'$  to another substance  $S$  to which they have greater affinity. In such a way *racemic bases* may be separated by means of an optically active *acid*, or *racemic acids* by means of an optically active *base*. This method is however not restricted to these two classes of compounds.

In later times Erlenmeyer<sup>2)</sup> and Neuberg<sup>3)</sup> have extended the method to condensation-processes with optically active aldehydes, nitrogen-compounds (*hydrazine-derivatives*); etc. We will again return to those investigations afterwards.

§ 8. Pasteur's first fission of a racemoid according to the method described, was the fission of the *racemic acid* itself into the *tartaric acids* by the aid of the dextrogyratory base *cinchonine*<sup>4)</sup> Later he did this by means of *quinicine* and *cinchonidine*, which bases are both dextrogyrate also. From the solution, the *cinchonidine*-

<sup>1)</sup> W. J. Pope and S. J. Peachy, Journ. Chem. Soc. London **75**. 1066. (1899).

<sup>2)</sup> E. Erlenmeyer Jr., Ber. d. d. Chem. Ges. **36**. 976. (1903).

<sup>3)</sup> C. Neuberg, Ber. d. d. Chem. Ges. **36**. 1192. (1903).

<sup>4)</sup> L. Pasteur, Compt. rend. **36**. 191. (1852); Ann. de Chim. et Phys. (3). **38**. 437. (1853).

*l*-tartrate crystallises first, being less soluble than the corresponding *d*-tartrate. If *quinicine* be used, the *right tartrate* crystallises first. Since that time numerous fissions of racemic acids by means of optically active bases have been made: the bases used were chiefly natural alcaloids, as: *strychnine*, *brucine*, *morphine*, *quinine*, *cinchonine*, *cinchonidine*<sup>1)</sup>, etc., and more recently bases such as:  $\alpha$ -*phenyl-ethyl-amine*<sup>2)</sup>, *hydroxy-hydrindamine*<sup>3)</sup>, etc. On the other hand, many racemic bases are resolved by means of optically active acids: *d*-tartaric acid, *l*-malic acid, and since 1898, — when Pope and Peachy<sup>4)</sup> introduced some strongly optically active *camphor*-derivatives for that purpose, — especially by means of the *camphor-sulphonic*, and the *chloro*-, resp. *bromo-camphor-sulphonic acids*.

Thus *lactic acid*:  $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ , was separated by Jungfleisch<sup>5)</sup> by means of *quinicine*, and by Purdie and Walker<sup>6)</sup> by means of *strychnine*.

Lovén<sup>7)</sup> separated  $\alpha$ -*phenyl-ethyl-amine* by means of *l*-malic acid, while Pope and Read<sup>8)</sup> made this fission by condensation with *d*-oxymethylene-camphor. Ladenburg<sup>9)</sup> in his famous synthesis of *coniine*, was able to separate the obtained inactive base into its optically active components by means of *d*-tartaric acid, while Pope and Read<sup>10)</sup> resolved *hydroxy-hydrindamine* by means of the active  $\alpha$ -*bromo-camphor- $\pi$ -sulphonic acid*. The *tri-ethylene-diamine-cobalti-bromide*:



was resolved into its optically active components by Werner<sup>11)</sup> by means of its *d*-bromo-tartrate, and the same method can be used

1) L. Pasteur, Jahresber. f. Chem. (1860), p. 250.

2) W. J. Pope and J. Read, Journ. Chem. Soc. London **95**. 172. (1909); **103**. 451. (1913); J. M. Lovén, Ber. d. d. Chem. Ges. **29**. 2313. (1896); W. Marckwald and R. Meth, ibid. **38**. 801. (1905).

3) W. J. Pope and J. Read, Journ. Chem. Soc. **99**. 2071. (1911); **101**. 758. (1912); **103**. 447. (1913).

4) W. J. Pope and S. J. Peachy, Journ. Chem. Soc. **73**. 893. (1898); F. S. Kipping and W. J. Pope, ibid. **63**. 548. (1893).

5) E. Jungfleisch, Compt. rend. **139**. 56. (1904).

6) T. Purdie and J. W. Walker, Journ. Chem. Soc. London **61**. 754. (1892).

7) J. M. Lovén, Journ. f. prakt. Chemie (2). **72**. 307. (1905).

8) W. J. Pope and J. Read, Journ. Chem. Soc. **103**. 451. (1913).

9) A. Ladenburg, Ann. der Chemie **247**. 85. (1886).

10) W. J. Pope and J. Read, Journ. Chem. Soc. London **101**. 758. (1912).

11) A. Werner, Ber. d. d. Chem. Ges. **45**. 121. (1911); F. M. Jaeger, Proceed. Kon. Akad. van Wet. Amsterdam, **17**. 1271. (1915).

in the case of the corresponding *rhodium*-salt.<sup>1)</sup> The latter, and also the corresponding *chromi*-salt, may be separated also by the aid of *sodium-d-camphor-nitronate*<sup>2)</sup>, while *potassium-rhodium-oxalate*, and the corresponding *chromi*-salt<sup>3)</sup>, can be split by means of *strychnine*<sup>4)</sup>. The very strongly rotating components of these salts themselves can in their turn be used for the fission of externally compensated organic compounds; thus Werner and Basyrin<sup>5)</sup> succeeded in separating the racemic  $\alpha$ - $\alpha'$ -*dimethyl-succinic acid*:  $\text{COOH}.\text{CH}(\text{CH}_3).\text{CH}(\text{CH}_3).\text{COOH}$ , which till then had not been resolved by any other means, into its antipodes by the aid of the optically active *tri-ethylenediamine-cobalti*-salt. The number of these examples can easily be augmented. A review of fissions made up to 1894 was given by Winther<sup>6)</sup>, while numerous instances can be found in all larger works on stereochemistry, thus in that of Bischoff-Walden<sup>7)</sup>, that of Werner<sup>8)</sup>, etc. Since the number of experiments in this direction has increased very rapidly.

The application of the method is universal, but in every case the difficulty is the choosing of the optically active compound suited for the purpose. Everything depends upon the finding of favorable solubility-relations between the newly formed compounds: commonly the greater the difference in solubility is, the better the fission will succeed. Moreover suitable conditions for crystallisation play an important rôle in this; often the compounds formed can only be obtained as syrups, or do not form well developed crystals. Every one who has had occasion to make experiments of this kind, knows the disillusioning obstacles often presented to him and the serious difficulties to be overcome.

§ 9. Attention must be drawn to another difficulty which may crop up, namely, that the optically active component often does not combine directly with each of the two active components contained in the racemoid separately, but with *the whole racemic compound* as such, which combination then above or below a certain transition-temperature may be changed into a mixture of the two different

1) A. Werner, Ber. d. d. Chem. Ges. **45**. 1228. (1912).

2) A. Werner, *ibidem*.

3) A. Werner, Ber. d. d. Chem. Ges. **45**. 865. (1912).

4) A. Werner, Ber. d. d. Chem. Ges. **47**. 1954. (1914); **45**. 3061. (1912).

5) A. Werner and M. Basyrin, Ber. d. d. Chem. Ges. **46**. 3229. (1913).

6) Ch. Winther, Ber. d. d. Chem. Ges. **28**. 3000. 1895).

7) C. A. Bischoff and P. Walden, *Handbuch der Stereochemie*, (1894).

8) A. Werner, *Lehrbuch der Stereochemie*, Jena, (1904).

compounds which are contained in it. The behaviour of such a *partial racemic* compound, as it is called, is then quite analogous to that of a racemic compound above or below its transition-temperature, except that the typical symmetry of the solubility-relations is lost, because the pseudo-racemic compound no longer splits up into components which are mirror-images of each other.

The first example of this kind was found by Ladenburg<sup>1)</sup> in the case of *strychnine-racemate*, and of the salt formed from *quinine* and *methylsuccinic acid*. The first substance appears at 30° C. to have a (maximum) transition-temperature. Above 30° C. therefore it is split up into *strychnine-d-tartrate* and *strychnine-l-tartrate*.

The solubility-relations existing in such cases were first fully understood and explained by Bakhuis Roozeboom<sup>2)</sup>. The symmetry of our former figures is of course now lost (*fig. 159*), while the solubility-curve *TS* for the mixture no longer coincides with *OA*, because

of the difference in solubility of the dextro-, and laevogyrotory component. *QT* might even lie wholly to the right of *OA*, and in that case the temperature-range *MT* in which no solutions of the pure racemoid can exist, will become yet greater, the racemoid being continually decomposed by gradual precipitation of the laevogyrotory salt, until at the transition-temperature corresponding to *T*, the fission is finally completed.

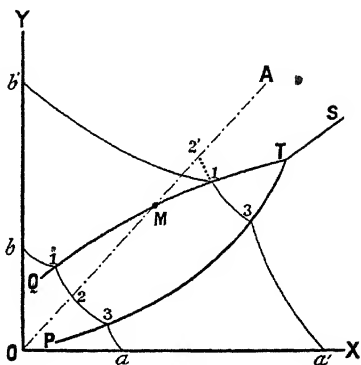


Fig. 159.

1) A. Ladenburg and collaborators: Ber. d. d. Chem. Ges. **27**. 75. (1884); **31**. 524, 937, 1969. (1898); **32**. 50. (1899); **36**. 1649. (1903); **40**. 2279. (1907); **41**. 966. (1908); Ann. der Chemie **364**. 227. (1909); E. Fischer, Ber. d. d. Chem. Ges. **27**. 3225. (1894). F. S. Kipping, Journ. Chem. Soc. London **95**. 408. (1909); M. Levi-Malvino and A. Mannino, Atti Rend. Acad. Lincei Roma (5). **18**. II. 144. (1909); A. Windaus and C. Resau, Ber. d. d. Chem. Ges. **48**. 861. (1915). F. W. Küster, Ber. d. d. Chem. Ges. **31**. 1847. (1898). A. Findlay and E. M. Hickmans, Journ. Chem. Soc. London, **91**. 905. (1907); **95**. 1386. (1909). H. Dutilh, Proceed. Kon. Acad. v. Wet. Amsterdam, **12**. 393. (1910).

2) H. W. Bakhuis Roozeboom, Zeits. f. phys. Chemie **28**. 502. (1899).



Of course the solution which corresponds to this transition-temperature, does in general not necessarily contain equal quantities of the dextro- and laevogyrotory compounds; this can only be the case approximately when the difference of their solubilities at the temperature under consideration is very slight.

If the splitting-up of the partial racemate does *not* occur, or cannot be produced in some way, partial racemism may therefore also be an obstacle for the successful fission of a racemoid by this method. Many cases of partial racemism have since been observed: '*strychnine-racemate*, *tetrahydro-papaverine-d-tartrate* <sup>1)</sup>, *l-menthyl-mandelic ether* <sup>2)</sup>, etc.

Ladenburg <sup>3)</sup> found for  $\beta$ -*pipecoline-bitartrate* a partial racemism at higher temperatures, while a fission occurred at lower temperatures. For *brucine-biracemate* <sup>4)</sup> a transition-temperature of 50° C. was found, *below* which the partial racemate can exist, while at higher temperatures fission takes place. Levi-Malvano and Mannino found partial racemism with some *santonine-salts* <sup>5)</sup>, while Windaus und Resau <sup>6)</sup> met with a partial racemic compound in the case of  $\beta$ -*cholestanol* and *pseudo-coprosterol*. The number of such increases from year to year.

§ 10. III. The third method of fission also proposed by L. Pasteur <sup>7)</sup>, is that by means of living organisms, by *bacteria*, *moulds*, *yeasts*, and by a number of very complicated organic substances belonging to the proteids, and being named *ferments* or *enzymes*.

Pasteur <sup>7)</sup>, as is well known, was engrossed by the idea that the production of single optically active substances was the very prerogative of life. To this view of vitalism, which supposes that in vital agency, special asymmetric forces play a directional rôle, a number of experiments must be referred, made by him in later years, and which were as unsuccessful as all other attempts made since then

<sup>1)</sup> W. J. Pope and S. J. Peachy, Zeits. f. Kryst. u. Min. **31**. 11. (1900); Journ. Chem. Soc. London, **73**. 902. (1898).

<sup>2)</sup> A. Findlay and E. M. Hickmans, Journ. Chem. Soc. London **91**. 909. (1907).

<sup>3)</sup> A. Ladenburg, Ber. d. d. Chem. Ges. **27**. 75. (1884).

<sup>4)</sup> A. Ladenburg, Ber. d. d. Chem. Ges. **40**. 2279. (1907).

<sup>5)</sup> M. Levi-Malvano and A. Mannino, Atti Rend. Acad. Lincei Roma (5). **18**. II. 144. (1909).

<sup>6)</sup> A. Windaus and C. Resau, Ber. d. d. Chem. Ges. **48**. 861. (1915).

<sup>7)</sup> L. Pasteur, Compt. rend. de l'Acad. d. Sc. Paris, **32**. 110. (1851); **36**. 26. (1853); **37**. 110, 162. (1853); **51**. 298. (1860).

by a number of chemists, directly to produce an optically active substance from an inactive material by mere chemical action. In the next chapter we shall return to these interesting and fundamental questions in detail; it suffices here to point out the fact that guided by this preconceived idea, Pasteur started to investigate more accurately the action of various moulds on solutions of *calcium-* and *ammonium-racemates*, after he had accidentally observed that these can grow in them. He tried to answer the question, as to what would be the behaviour of the two components of the racemate under the influence of the living organism.

He found that the originally inactive solution became gradually *laevogyrotory*; the organism (*Penicillium glaucum*) had evidently selected for its nutriment that form of the *tartaric acid*-molecule which suited best its particular needs. Although this selective consumption of one of the antipodes by living organisms has been often found, it must however be recognised that the selective fermentations as a general phenomenon, have not yet been studied in a sufficiently systematic way <sup>1)</sup>. In numerous cases we do not know whether the culture used was of only one species, nor to what species the organisms belonged in many cases. Neither is there certainty as to whether the organism merely decomposes one active component of the mixture *more rapidly* than the other, or whether it leaves one of them entirely intact. Most probably there is only a great difference of rate of velocity.

It may be thought most remarkable, that such a relatively minute difference between two molecules should be sufficient to cause such a fundamental difference in the behaviour of a living organism if brought into contact with it. More recent experiments however have not only proved this fact beyond all doubt, but from E. Fischer's work <sup>2)</sup> on the selective fermentation of sugars under the action of yeasts, it seems probable that the action of every living organism corresponds to only a definite, very exclusive, special arrangement of the atoms in the chemical molecules.

However in recent times serious doubt has arisen, as to whether the specificity of the action of organisms, as brought to the fore by Fischer, and illustrated by his image of *lock* and *key*, should

<sup>1)</sup> As an interesting contribution however, see: W. Pfeffer, *Jahrb. f. wiss. Botanik*, **28**. 205. (1892).

<sup>2)</sup> E. Fischer and collaborators, *Ber. d. d. Chem. Ges.* **27**. 2031, 2985, 3228, 3479. (1894); **28**. 1429, 1508, 3031. (1895); *Zeits. f. physiol. Chemie* **26**. 60. (1898).

be maintained. The way for further investigations should be left open, but at any rate it seems nearer to the truth to suppose that only *great differences in speed of activity* take place<sup>1)</sup>. Indeed the experiments of Neuberg<sup>2)</sup> on the action of bacteria, and those of Pringsheim<sup>3)</sup> on that of moulds, on racemoids, seem strongly to confirm the last view.

That from a physiological point of view there are undeniable differences in the behaviour of living organisms towards enantiomorphously related substances with which they are brought in contact, is proved quite conclusively, and the same is the case also for the human organism. Thus Piutti<sup>4)</sup> already drew attention to the fact that of both the isomeric optically active *asparagines* the one component is sweet, the other insipid; and Menozzi and Appiani<sup>5)</sup> found the same fact in the case of *glutaminic acid*. Poulsson<sup>6)</sup> observed that from the *racemic polypeptides* twice as much was necessary for nutrition, as when the optically active form was used, while *laevogyrotory nicotine* (from tobacco) is twice as toxic as the synthetic *dextrogyrotory* alcaloid. Artificial *adrenaline* is much less active than is the natural product, which is endowed with rotatory power. The mydriatic action of *atropine* upon the pupil of the eye is apparently specific for the natural base, while its mirror-image does *not* show this property. The dextrogyrate *cocaine* seems to paralyse the nerves of the tongue much more rapidly than the laevogyrate alcaloid does. From this and similar examples it is evident that in the assimilation-process of higher animals also, enantiomorphously related molecules are by no means equivalent.

Pasteur himself gave an explanation which, if followed, enables us to bring this phenomenon within the scope of the arguments given in the foregoing paragraphs referring to the second method of fission. According to Pasteur's view, this selective action must, beyond any doubt, depend on the dissimilar interaction of asymmetric

1) K. Fajans, Zeits. f. phys. Chemie **73**. 25; **75**. 232. (1910).

2) C. Neuberg, Biochem. Zeits. **18**. 431. (1909).

3) H. Pringsheim, Zeits. f. physiol. Chemie. **65**. 96. (1910).

4) A. Piutti, Compt. rend. de l'Acad. d. Sc. Paris, **103**. 134. (1886); L. Pasteur, *ibid.* p. 138.

5) A. Menozzi and G. Appiani, Atti R. Acad. Lincei (5) **2**. II. 421. (1893).

6) E. Poulsson, Archiv. exp. Path. u. Pharm. **27**. 309. (1890); *Ion*, **2**. 188. (1910). Cf. also: C. Neuberg and J. Wohlgemuth, Ber. d. d. Chem. Ges. **34**. 1745. (1901); Zeits. f. physiol. Chemie **35**. 41. (1902); P. Mayer, Bioch. Zeits. **1**. 39. (1906).

bodies contained in the cells of living organisms, with the molecules of both active components. Thus the different action of the dextro- and laevogyrate *asparagines* on the tongue, would be caused by the different chemical action of both antipodes upon an asymmetric substance present in the tissue of the gustatory nerve.

The living organism thus uses the one component of the externally compensated mixture or compound, because its physiological action has been adapted to a special nutriment; and to the same cause must also be attributed the different action on the human body of *nicotines*, *atropines*, and *adrenalines* which have another configuration than the natural products.

These views have become most probable, since Buchner<sup>1)</sup> proved that from yeast-cells by grinding and crushing them with sand, after filtration a clear juice could be obtained from which a special ferment, *zymase*, could be isolated, which produces fermentation as well as the living cells themselves, and that a second sugar-inverting ferment, *invertase*, known even then, is also present in the cells. As *zymase* and *invertase* are life-less chemical substances, the view that the special phenomena of fermentation are *not directly* connected with the life-process itself, but can be produced by such characteristic substances present in the cells, has now become certain.

Fischer<sup>2)</sup> confirmed that  $\alpha$ -methyl-glycoside is decomposed by *invertase*, while  $\beta$ -methyl-glycoside is not; with *emulsine* however just the reverse occurs. The enzyme thus has undoubtedly a "selective" action, in the same way as this was formerly stated in the case of living organisms. This apparently selective action must most probably also be referred to a great difference in the velocity of action, when several enzymes are made use of for the attack of the same kind of substances.

Dakin<sup>3)</sup> found that *lefthanded benzyl-mandelic ether* is much more rapidly hydrolysed by *lipase* (from the liver), than the dextrogyratory antipode, and that in general the ethers of optically active

1) E. Buchner, Ber. d. d. Chem. Ges. **30**. 117, 1110, 2668. (1897); **31**. 209, 568. (1898); **33**. 3307, 3311. (1900); E. Buchner and R. Rapp, *ibid.* **31**. 1084, 1090. (1898); **32**. 127, 2086. (1899); **34**. 1523. 1901); E. Buchner and A. Spitta, *ibid.* **35**. 1703. (1902); E. Buchner and W. Antoni, Zeits. f. physiol. Chem. **44**. 206. (1905); **46**. 136. (1905); etc.

2) E. Fischer, Ber. d. d. Chem. Ges. **27**. 2985, 3230, 3479. (1894); **28**. 1429, 1508, 3031. (1895).

3) H. D. Dakin, Journ. of Physiol. **30**. 253. (1904); **32**. 199. (1905); cf. also: A. Mac Kenzie and A. Harden, Proceed. Chem. Soc. London, **19**. 48. (1903).

acids are, in both enantiomorphous configurations, decomposed by it with very differing velocities; the differences in velocity can amount to 50% and 130% of the values observed in the case of the other antipode.

Herzog and Meier<sup>1)</sup> stated that mould-cultures, after being killed by means of acetone or methyl-alcohol, will oxidize dextrogyratory *tartaric acid* much more rapidly than the laevogyratory isomeride, and the same appeared to be the case with other oxyacids, although not to so high a degree. A similar difference in velocity of attack was found by Abderhalden and Pringsheim<sup>2)</sup> if the juice of squeezed-out cells of *Aspergillus Wentii*, or of *Allenheria Gayoni* were used for the decomposition of *polypeptides*, like *leucylglycine* into their optically active forms. After this, it can hardly be doubted any longer that of the "specific" attack of living organisms or of enzymes, a common explanation can as a matter of fact be given, and that this must be considered to consist in the differences in *velocity* of attack only.

Most of these reactions appear intrinsically to be true reversible or semi-reversible reactions<sup>3)</sup>: thus *glycose* is changed by *maltase* into *maltose* (or rather into *iso-maltose*)<sup>4)</sup> in this way; *kefir-lactase* acting on a mixture of *glycose* and *galactose*, produces *iso-lactose*, etc. The same is true for the action of *lipase*, of *emulsine*, and of a number of other animal or vegetable enzymes.

The close analogy with the effect of yeasts on sugars, formerly stated by Fischer<sup>5)</sup>, is evident; thus from *i-glycose* the *lefthanded* component may for instance be obtained by means of yeast, because yeast attacks the *d-glucose*, while it does not attack the *l-glycose*, or only to an unappreciable extent, during the same time; in the same way as in Pasteur's original experiments the *d-ammonium-tartrate* was attacked almost exclusively by *Penicillium glaucum*

<sup>1)</sup> R. O. Herzog and A. Meier, Zeits. f. physiol. Chem. **59**. 57. (1909).

<sup>2)</sup> E. Abderhalden and H. Pringsheim, Zeits. f. physiol. Chem. **59**. 249. (1909); cf. also: G. Bredig and K. Fajans, Ber. d.d. Chem. Ges. **41**. 752. (1908).

<sup>3)</sup> Literature on the *reversibility of enzyme-action*; A. Croft Hill, Journ. Chem. Soc. London, **73**. 634. (1898); **83**. 578. (1903); J. H. Kastle and A. S. Loevenhart, Amer. Chem. Journal **24**. 491. (1900); M. Hanriot, Compt. rend. de l'Acad. d. Sc. Paris **132**. 212. (1901); H. Pottévin, Compt. rend. **136**. 767. (1903); E. Bourquelot and M. Bridel, Ann. de Chim. et Phys. **28**. 145. (1913); W. M. Bayliss, Journ. Physiol. **36**. 221. (1907); **43**. 455. (1912); **46**. 236. (1913).

<sup>4)</sup> E. Fischer, Ber. d.d. Chem. Ges. **32**. 3617. (1899); Zeits. f. physiol. Chemie. **26**. 60. (1898); E. Fischer and E. F. Armstrong, Ber. d.d. Chem. Ges. **35**. 3144. (1902).

<sup>5)</sup> E. Fischer, Ber. d.d. Chem. Ges. **23**. 2620. (1890).

during warm weather, but not the laevogyrotory salt. It happens in many cases, that if a substance can be fermented both by *emulsine* and by *invertase*, the behaviour of both enzymes towards the antipodes is just opposite. Whether this may be considered to be a general rule, is not sure. Fischer stated that all enzymes fermenting *maltose*, act in the same way on  $\alpha$ -*glucosides* <sup>1)</sup>.

Of course the disadvantage of this method of fission is that half of the material is destroyed, only one of the optically active components being preserved. Moreover the substances must be such that living organisms can grow in their solutions, while just because of the exclusively selective action, it is often a difficult matter to find the right organism to effect the desired separation.

§ 11. Although in the next chapter we shall return to the details of the method, a few words must again be said on a fission-method, as used by some investigators, which is founded on the differences in the *velocity of formation or decomposition* of compounds of the types *Af* and *A'f*.

Marckwald and Mac Kenzie<sup>2)</sup> succeeded, after a number of unsuccessful experiments of other investigators<sup>3)</sup>, in demonstrating that if  $\alpha$ -*ethoxy-propionic acid*, *racemic mandelic acid*, etc., be combined with *l-menthol* to form an ether, and if the reaction be stopped after a certain lapse of time insufficient to finish the change completely, the acid set free from the ether by saponification was endowed with rotatory power.

The same appeared to be the case if *racemic mandelic acid* were heated with *l-menthyl-amine*, so as to form the corresponding *amide*. In the portion which was not changed into amide, an excess of the laevogyrotory acid was found to be present. It should be noted that the compound which was formed more rapidly by etherification, appeared also to be more rapidly decomposed by saponification, which is in accordance with the fact that we have to deal here with a reversible action, leading to a state of final equilibrium.

This fission of the racemoid is of course only a *partial* one. We shall return to this subject in the next chapter, when we are

1) E. Fischer, Zeits. f. physiol. Chemie 26. 69, 79. (1898).

2) W. Marckwald and Mackenzie, Ber. d.d. Chem. Ges. 32, 2130. (1899); 34. 469. (1901); W. Marckwald and R. Meth, Ber. d.d. Chem. Ges. 38. 801. (1905).

3) L. Simon, Bull. de la Soc. Chim. (3). 11. 760. (1894); P. Frankland and Th. S. Price, Journ. Chem. Soc. London, 71. 253. (1897); etc.

dealing with the problem of asymmetric synthesis in general.

§ 12. Till now we have dealt only with those cases in which either an externally compensated mixture of both components or a true racemic compound of them was present.

However another difficulty for obtaining the two components in a perfectly pure state is, besides the obstacles already mentioned, this, that the two components may occasionally form together an *uninterrupted series of mixed-crystals*, this series behaving therefore as a single solid phase of continually varying composition.

This phenomenon discovered in 1897 by Kipping and Pope <sup>1)</sup> in the case of some *camphor*-derivates, was named *pseudo-racemism*. Since Bakhuis Roozeboom <sup>2)</sup> in 1899 published the paper in which he indicated the way to discriminate with certainty the three classes: *racemic compounds*, *externally compensated mixtures*, and *pseudo-racemic mixed-crystals*, the pseudo-racemic mixtures too have been the subject of some investigations <sup>3)</sup>; however it is very necessary in this case also, that more extended and systematic researches be made to further our rudimentary knowledge in many directions.

Kipping and Pope <sup>4)</sup> described the *trans- $\pi$ -camphanic acid* as a first example of such pseudo-racemic mixtures; the active and inactive substances have very similar crystal-forms and appearance:

*Active*: Monoclinic;  $a : b : c = 1,9110 : 1 : 1,4627$ ;  $\beta = 69^{\circ}5'$

*Inactive*: Monoclinic;  $a : b : c = 1,8105 : 1 : 1,4502$ ;  $\beta = 67^{\circ}41'$

The same was the case with the active and inactive *trans-camphotricarboxylic-anhydride*. They come to the conclusion that the crystals of the inactive substance are *not homogeneous*, but merely complicated intercalations of crystals of the *d*- and *l*-components; the bad reflexes of the light on some facets, observed during the measurements, their striation, etc., remind us very much of similar peculiarities, met with in mixed-crystals, and in crystalline aggregations as, for instance, are found in some *amethyst*-crystals. The angular values of inactive and active crystals are very analogous; small but per-

<sup>1)</sup> F. S. Kipping and W. J. Pope, Journ. Chem. Soc. London **71**. 973. 989. (1897).

<sup>2)</sup> H. W. Bakhuis Roozeboom, Zeits. f. phys. Chemie **28**. 494. (1899).

<sup>3)</sup> J. H. Adriani, Akad. Proefschrift, Amsterdam, (1900); Zeits. f. phys. Chemie **33**. 453. (1900); **36**. 168. (1901); Proceed. Kon. Akad. v. Wet. Amsterdam **9**. 438. (1900); J. Minguin and E. G. de Bollemont, Compt. rend. de l'Acad. d. Sc. Paris **132**. 1573. (1901); J. Minguin, Bull. d. l. Soc. Chim. (3). **27**. 888. (1902); Compt. rend. **124**. 86. (1897).

<sup>4)</sup> F. S. Kipping and W. J. Pope, Journ. Chem. Soc. London **69**. 931. (1896); etc.

fectly distinct differences however are actually present, which the authors mentioned attribute to the disturbing effect of the intercalation.

In so far such pseudo-racemic mixtures appear closer related to the so-called layer-crystals than to the true homogeneous mixed-crystals between strictly isomorphous salts.

Ostromisslensky<sup>1)</sup> considers the formation of pseudo-racemic mixtures from the *d*- and *l*- components as a transformation of the antipodes into a second, dimorphic and holohedral modification. Pseudo-racemic mixed-crystals can only form an *uninterrupted* series of mixtures; however Ostromisslensky thinks it possible that the active antipodes eventually form solid solutions with a racemic compound, in the same way as some compounds can be homogeneously mixed to some extent with their products of dissociation. The racemic compounds would never crystallise in forms differing from their mirror-images. And finally he draws attention to the fact that in contradiction to Gernez' views<sup>2)</sup>, *triboluminescence* may be used as a criterion to discriminate between an externally compensated mixture and a true racemic compound. If the active form shows triboluminescence, the racemic compound does *not*; at the transition-temperature of a mixture, the phenomenon of triboluminescence suddenly disappears. Further investigation of these relations seems to be highly desirable.

As further examples of this kind, Kipping and Pope mention the *d*- and *l*-camphorsulphonic-chlorides, and the corresponding bromides<sup>3)</sup>; *carvoxime*<sup>4)</sup>; *dipentene-tetrabromide*<sup>5)</sup>; *ω*-bromo-camphoric-anhydride<sup>6)</sup>; *carvon-tribromide*<sup>7)</sup>, etc. Among Minguin's *camphor*-derivatives<sup>8)</sup> there are certainly some beautiful examples of this kind too.

1) I. Ostromisslensky, Journ. d. russ. phys. chem. Ges. St. Petersburg 42. 102, 606. (1910).

2) D. Gernez, Compt. rend. de l'Acad. d. Sc. Paris 147. 11. (1908); L. Tschugajeff, Ber. d. d. Chem. Ges. 34. 1820. (1901).

3) F. S. Kipping and W. J. Pope, Journ. Chem. Soc. London. 63. 565. (1893); 67. 359. (1895).

4) P. Beyer, Zeits. f. Kryst. 18. 298. (1890); J. H. Adriani, loco cit.

5) C. Hintze, Ann. der Chemie 227. 278. (1885).

6) O. Aschan, Acta Soc. Scient. Fenn. 21. (V). 193. (1896); F. J. Wiik, ibid. 203, 205. (1896).

7) Th. Liebisch, Ann. d. Chemie, 286. 142. (1895).

8) J. Minguin, loco cit.



If Bruni's<sup>1)</sup> suspicion be right that the so-called "double-salt" of *d-ammonium-tartrate* and *l-ammonium-malate*, described by Pasteur<sup>2)</sup>, be really a mixed-crystal, we should have here an object intermediate between a pseudo-racemic mixed-crystal and a partially-racemic compound, as defined by Fischer<sup>3)</sup>, who draws attention to the fact that both salts are only antipodes with respect to one half of their molecule. The corresponding *d-tartaric acid* and *l-malic acid* themselves do not form such a double compound or pseudo-racemic mixture. Fischer proposes to give in that case a special name to the phenomenon stated above, and to call it *partial pseudo-racemism*. However, here also it appears very desirable to make more investigations in this direction to establish the real occurrence of such "partial" pseudo-racemism beyond all doubt.

Beautiful examples of true pseudo-racemism were further found by Marckwald and Nolda<sup>4)</sup> in the case of active *amyl*-derivatives: 1-, and 2-*amyl*-3-nitro-*phtalic ethers*; *barium-act.amyl-sulphate* (+ 2H<sub>2</sub>O); *act.amyl-carbamate*; etc. Finally by Riiber<sup>5)</sup> in the case of dextro- and laevogyrate  $\beta$ -*phenyl-glyceric acid* (mpt.: 141° C.).

As the components of such mixed-crystals in general cannot be separated completely by repeated crystallisations, — at least if the number of these be not infinitely great, or in practice: exceedingly great, — a separation will certainly not be reached in our case, where the solubilities of both components are equal. Therefore *pseudo-racemism* may also be mentioned amongst the serious obstacles eventually met with in the fission of racemoids into their optically active components<sup>6)</sup>.

§ 13. A phenomenon often observed in working with optically active substances is, that the rotatory power of such a solution especially if it be heated to a higher temperature, gets gradually smaller and smaller until finally it has become *inactive*. The velocity of this change can vary within wide limits: there are solutions which even on boiling preserve their rotatory power completely, but there are also cases where it is destroyed within a few minutes. Thus

1) G. Bruni, in: W. Meyerhoffer, Gleichgewichte der Stereoisomeren, (1906), p. 62.

2) L. Pasteur, Jahresberichte (1853), p. 417.

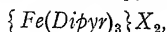
3) E. Fischer, Ber. d. d. Chem. Ges. 40. 944. (1907).

4) W. Marckwald and E. Nolda, Ber. d. d. Chem. Ges. 42. 1583. (1909).

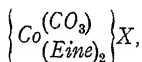
5) C. N. Riiber, Ber. d. d. chem. Ges. 48. 823. (1915).

6) W. J. Pope and J. Read, Journ. Chem. Soc. London, 97. 987. (1910).

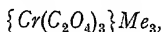
Werner<sup>1)</sup> observed that *tris-α-dipyridyl-ferro-salts* of the type:



lose half of their original, very high rotatory power in about half an hour; in the case of the *carbonato-di-ethylenediamine-cobalti-salts* <sup>2)</sup>:



it diminishes in about eight days and at room-temperature, to half its original value, while at 90° C. it is destroyed completely in a very short time. Also the complex *chromi-tri-oxalates* <sup>3)</sup>:



lose their rotatory power rather rapidly, in aqueous solution much faster than in a mixture of *acetone* and *water*.

Undoubtedly the mechanism of this reaction includes an intermediate stage of temporarily detaching of the groups from the central metal-atom. The already mentioned *tri-ethylenediamine-cobalti-*, and the corresponding *rhodium-salts* however, can be boiled in solution without the rotatory power of it perceptibly diminishing.

On closer examination it is found that the phenomenon described is really connected with the reaching of a state of equilibrium between the two enantiomorphously related molecules in the solution, equilibrium being arrived at if the molecules of both components be present in *equal* number.

The phenomenon mentioned is called *racemisation* or *auto-racemisation* <sup>4)</sup>. It can be also a serious obstacle in the attempts to produce the optical antipodes from a racemoid, and give many difficulties during the study of optically active substances.

That this is really a case which is wholly comparable with other cases of thermal equilibrium <sup>5)</sup>, could be demonstrated, among other ways, by the auto-racemisation of the ethers of optically active *bromo-succinic acid* <sup>6)</sup>. Walden found for instance, that dextrogyratory

1) A. Werner, Ber. d. d. Chem. Ges. **45**. 434. (1912).

2) A. Werner and Mac Cutcheon, Ber. d. d. Chem. Ges. **45**. 3283. (1912).

3) A. Werner, Ber. d. d. Chem. Ges. **45**. 3065. (1912).

4) A rigorous distinction between racemisation and auto-racemisation can not be made.

5) J. A. Le Bel, Compt. rend. **87**. 213. (1878); Bull. d. 1. Soc. Chim. (2). **31**. 104. (1879); J. Lewkowitsch, Ber. d. d. Chem. Ges. **15**. 1505. (1882).

6) P. Walden, Ber. d. d. Chem. Ges. **31**. 1416. (1898). Cf. also: J. H. Van 't Hoff, Vorles. ü. theor. u. phys. Chemie II. p. 122. (1899).

*dimethyl-bromo-succinate* lost its activity at ordinary temperatures in about four years, the dextrogyratory *isobutyl-bromo-propionate* and the corresponding *methyl-phenyl-bromo-acetate* in three years, while in the case of the ethers of *hydroxy-* or *chloro-acids*, the auto-racemisation took place much less rapidly. At higher temperatures the process is appreciably accelerated.

Because the system no longer alters with varying temperature, when optical inactivity is once established, the heat-effect of the change of an atomistic configuration into its enantiomorphous one must be zero. There is moreover every reason to suppose that in the reversible reaction:  $d \rightleftharpoons l$ , the velocity-constants  $k$  and  $k'$  of both opposite changes are equal. The kinetic equation, expressing the relation between the time  $t$  elapsed and the quantity transformed, may be written:

$$\frac{dx}{dt} = k(a-x) - k'x = k(a-2x),$$

which on integration gives:

$$\frac{1}{t} \ln \frac{a}{a-2x} = \text{constant}.$$

From measurements made by Gadamer<sup>1)</sup> on the racemisation-velocities of *hyoscyamine* and of *scopolamine* under the influence of *sodium-hydroxide* and of *tropine* respectively, Herz<sup>2)</sup> calculated the racemisation-constants from this equation; he found for *hyoscyamine* (at 5° C.) with *sodium-hydroxide*:  $6.5 \cdot 10^{-3}$ , with *tropine*:  $2.2 \cdot 10^{-2}$ ; for *scopolamine* with *sodium-hydroxide*:  $0.77 \cdot 10^{-2}$ , and with *tropine*:  $1.9 \cdot 10^{-2}$  at 2° to 4° C.

Commonly racemisation is started by heating: the presence of some other substances, be it as a solvent or not, often seems to have an accelerating effect. Thus Jungfleisch<sup>3)</sup> found, that *tartaric acid* becomes more rapidly racemised if heated in the presence of some *aluminium-tartrate*, than if heated alone. Often racemisation occurs in an appreciable degree when a chemical reaction takes place; thus, for instance. Pope and Harvey<sup>4)</sup> demonstrated that dextrogyratory *a-c-tetrahydro-β-naphthylamine* became partially race-

1) J. Gadamer, Archiv der Pharmac. 239. 294. (1901).

2) W. Herz, Jahrb. der Schles. Ges. für vaterl. Kultur, Mai 1911.

3) E. Jungfleisch, Compt. rend. de l'Acad. d. Sc. Paris 85. 805. (1877).

4) W. J. Pope and A. W. Harvey, Journ. Chem. Soc. London 79. 74. (1901); Proc. Ch. Soc. 16. 74, 206, (1890).

mised, while it was transformed into the *acetyl*-, *benzoyl*-, or *benzylidene*-derivatives. Fischer<sup>1)</sup> observed that if *trimethylamine* re-acts with dextrogyratory *ethyl- $\alpha$ -bromo-propionate*, the *ethyl-trimethylamino-propionate* produced racemises more rapidly if the quaternary ammonium-salt is present. Marckwald and Nolda<sup>2)</sup> found that *d-amyl-bromide* is much more rapidly racemised if *silver-acetate* be present, than if this is not the case.

The process of autoracemisation is very difficult to explain from the standpoint of the doctrine of directional valency-unities, as proposed by Van 't Hoff. A rational explanation was suggested in some cases by supposing intermediate tautomeric changes, e. g. in the cases where transitions from the "cetonic" into the "enolic" form and vice versa are possible. Another explanation was given by Werner<sup>3)</sup>, fitting in with his views on valency and affinity, by supposing a gradual increase of the amplitude of vibrating radicals round their equilibrium-positions in space, if the temperature becomes higher.

The consequent influence of the solvent can hardly be doubted, as already stated in the case of the complex *chromi-oxalates*. Nef<sup>4)</sup> sees a connection between the tendency for racemisation and the binding and loosening of *water*-molecules from active organic molecules containing hydroxyl-groups, under intermediate formation of unsaturated compounds.

By Von Halban<sup>5)</sup>, and by Fröhlich and Wedekind<sup>6)</sup>, it has been demonstrated by means of kinetic measurements, that in the case of optically active derivatives of pentavalent nitrogen, auto-racemisation is indeed intimately connected with an intermediate detachment of groups, and successive recombination with the plurivalent central atom. Here the active substance appears undoubtedly to be decomposed into a *tertiar amine* and an *alkyl-halogenide*, until a dynamical equilibrium is reached. It is easily understood therefore

1) E. Fischer, Ber. d. d. Chem. Ges. **40**. 5000. (1907).

2) W. Marckwald and E. Nolda, Ber. d. d. Chem. Ges. **42**. 1583. (1909).

3) A. Werner, Beiträge zur Theorie der Affinität und Valenz, Zürich, (1891).

4) J. U. Nef, Ann. der Chemie **335**. 191. (1904); Cf. also: O. Rothe, Ber. d. d. Chem. Ges. **47**. 843. (1914); P. Pfeiffer, *ibid.* **47**. 1586. (1914).

5) H. von Halban, Ber. d. d. Chem. Ges. **41**. 2417. (1908); Zeits. f. Elektrochem. **13**. 57. (1907).

6) E. Wedekind and E. Fröhlich, Ber. d. d. Chem. Ges. **38**. 3438. (1906); **40**. 1646 (1907); E. Wedekind and F. Paschke, Ber. d. d. Chem. Ges. **41**. 2659. (1908).

that the velocity of racemisation in these cases appears to be a constitutive property. Thus for instance the active normal *butyl-methyl-benzyl-phenyl-ammonium-iodide* appeared to racemise in *chloroform*-solution much more slowly than the corresponding *isobutyl*-derivative did under similar circumstances; and analogous results were obtained, if *bromoform* was used as a solvent. The reaction appeared to be mono-molecular, with a rather high temperature-coefficient.

§ 14. The general conclusions to which Pasteur finally arrived may be briefly summarised as follows:

1) If the atoms of a chemical molecule be "dissymmetrically" arranged, this molecular "dissymmetry" implies the possibility of the existence of two opposed configurations of the molecule. Both isomerides have the same chemical properties, but they are endowed always with equal, but oppositely directed rotatory power. The presence of molecular dissymmetry therefore reveals itself by this rotatory power of the molecules and is wholly determined by their chemical nature.

2) When the atoms of a chemical molecule are dissymmetrically arranged, it is at the same time betrayed by the occurrence of non-superposable crystalline forms with both isomerides.

Let us see now, in how far these general conclusions, which are generally considered as constituting Pasteur's law, are really justified and confirmed by experience.

In the first instance we may ask: when has a chemical molecule such a "dissymmetrical" arrangement of its atoms as to make the existence of two enantiomorphously related isomerides possible?

Pasteur himself does not speak very definitely about the special conditions under which this occurs, and he only postulates that the atomic configuration shall be "non-superposable" with its mirror-image.

The first attempt to give a more concrete explanation of these conditions was successfully made in 1874 by Van 't Hoff<sup>1)</sup> and Le Bel<sup>2)</sup>, who independently of one another introduced into chemical science the conception of the so-called "asymmetric atoms", and thus became the very founders of modern stereochemistry. For of

<sup>1)</sup> J. H. Van 't Hoff, Voorstel tot uitbreiding der tegenwoordig in de scheikunde gebruikte structuurformules in de ruimte, Utrecht, (1874); La Chimie dans l'Espace (1874); Die Lagerung der Atome im Raume, (1877).

<sup>2)</sup> J. A. Le Bel, Bull. de la Soc. Chim. Paris (2). 22. 377. (1874).

course, an explanation of this kind of phenomena must involve the primary supposition of a *stereometrical* arrangement of the atoms in the molecule, i.e. of the necessity of making use of *stereometrical*, instead of *plane* structural formulae for the representation of molecular composition and configuration.

As Van 't Hoff's method of demonstration appears more suitable for its purpose than Le Bel's, we shall chiefly use the former's in developing the following reasonings.

According to Van 't Hoff, the four valencies of the carbon-atom may be considered as forces issuing from the carbon-atom, and like "vectorial" quantities, determined by *magnitude* and *direction* in space. As to their *size*, we dare not hazard a guess, as nothing certain is known about it, and further it is highly probable that it varies considerably with the special nature of the groups connected with the carbon-atom. As to the *direction*, however, Van 't Hoff makes the simple supposition that in compounds in which the four carbon-valencies are saturated by four *identical* substitutes, the four forces are directed like the lines joining the centre of a regular tetrahedron with its corners. Thus the configuration of compounds such as *methane*:

$\text{CH}_4$ , *tetra-methyl-methane*:

$\text{C}(\text{CH}_3)_4$ , *carbon-tetra-iodide*:

$\text{CJ}_4$ , etc., may be represented

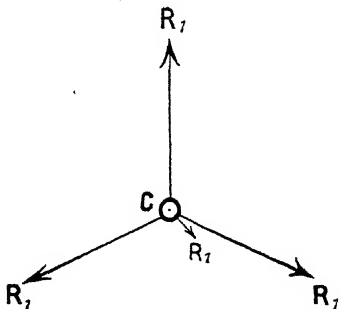


Fig. 160.

by a scheme such as in *fig. 160*. This arrangement of atoms possesses of course a high degree of symmetry: if the groups  $R_1$  be supposed to behave as substitutes having *spherical* symmetry, the whole arrangement possesses at least the symmetry of the group  $T^D$ . Indeed, the supposition that the groups  $R_1$  always behave in this respect as if they had the greatest possible symmetry, except in the case when they are non-superposable with their mirror-images, is of vital interest for the facts to be discussed in the following pages.

If for instance the group  $R_1$  were to be considered as fully asymmetrical, it might happen that the molecule as a whole had *no* planes of symmetry at all, and only axial symmetry. In that case, if no axes of the second order were present, the arrangement would cer-

tainly *differ* from its mirror-image, and two enantiomorphously related isomerides would also be possible in such a compound as

We shall consider such cases afterwards. But if the substitutes  $R_1$  do *not* differ from their enantiomorphous configurations, no isomerism of this kind has ever been observed, and therefore this fact can be used as an argument in proof of the hypothesis of the maximum symmetry of every such substitute in most cases. Van 't Hoff himself undoubtedly felt this: therefore he introduces into his theory the ideas about the special nature of the single, double, and threefold bond between atoms, and he supposes, amongst other things, that the radicals  $R_1$ , *if linked to the carbon-atom by a single tie*, can *freely rotate* round an axis coinciding with the direction of that bond. If  $R_1$  really rotates very quickly in the way just suggested, its properties will indeed appear as though it had a spherical symmetry of its own.<sup>1)</sup>

If now the same hypothesis be applied to *all* kinds of radicals which may eventually replace the group  $R_1$ , it is obvious that the rather high degree of symmetry of the arrangement suggested before, cannot be preserved if the four radicals are no longer equal.

The compound  $C(R_1)_3R'$  will have a symmetry which at the greatest could only be that of the group  $C_3^V$ ; and for a compound:  $C(R_1)_2(R')_2$  at the greatest it could be that of the group  $C_2^V$ .

A compound:  $C(R_1)_2R'R''$  can at the best have the symmetry of the group  $S$ , while a molecule:  $CR_1R'R''R'''$  has ordinarily no other symmetry than that of group  $C_1 (= A)$ , i.e., it does not possess any symmetry-properties at all. Such a molecule can therefore exist in two enantiomorphously related configurations, because it does

1) However, as already mentioned, the only exception to this is, when the substitutes  $R_1$ , which are linked to the central atom, are themselves of a configuration, which *differs* from its *mirror-image*. In such cases,  $R_1$  can be brought to coincidence with its mirror-image only by a reflection in a plane, or by an inversion, or most generally: by a rotation round an axis of the *second* order. The *asymmetric* substitutes  $R_1$  must therefore in all arguments bearing upon configurations of molecules in space, be denoted in the molecular formula by the symbols *d*- and *l*- (*dextro*- and *laevogyratory* respectively), to avoid confusion. Afterwards we shall consider a case, where the necessity of this becomes very evident.

Cf. on these topics also: W. J. Pope, Pres. Address to the Chem. Sect. of Brit. Assoc. for the Advanc. of Sciences, (1914).

not possess any symmetry-property of the second order whatever.

Van 't Hoff calls a carbon-atom, the four valencies of which are saturated by four *different* univalent atoms or radicals, an *asymmetric carbon-atom*. He was able to indicate the presence of at least *one* such asymmetric carbon-atom in all compounds which in the liquid or gaseous state exhibit the power of deviating

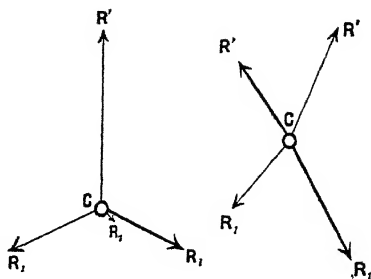


Fig. 161.

the plane of vibration of the polarised light. Since then, this hypothesis has proved valid in a great number of cases; and it was by this conception of the *plurivalent asymmetric atoms*, that a rational definition of the circumstances under which Pasteur's "molecular dissymmetry" was found, seemed to be given now, thus enabling the science of stereochemistry to be founded, as we know it to-day.

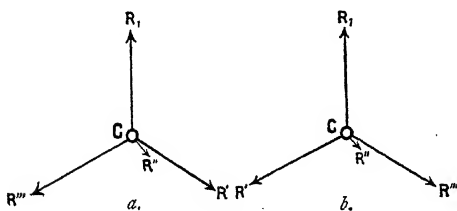


Fig. 162.

It should be remarked that by substituting for  $R_1$  other radicals  $R'$ ,  $R''$ ,  $R'''$ , etc., a gradual *distortion* of the molecule takes place: not only are the

distances of the radicals  $R_1$ ,  $R'$ ,  $R''$ ,  $R'''$ , etc. from the central carbon-atom undoubtedly *different*, but as a consequence of the mutual attractions and repulsions of the substitutes, the forces issuing from the carbon-atom will certainly deviate from those supposed in the case of *fig. 160*, — provided always that we accept the rather rough mechanical image proposed by Van 't Hoff. In the case of a compound:  $CR_1R'R''R'''$ , the "regular" tetrahedral arrangement of *fig. 160* will have quite disappeared; it will be replaced by a wholly *irregular* one. This must be firmly kept in mind, even though it should appear equally true that the two imaginary arrangements *a* and *b* in *fig. 162* would again seem to be enantiomorphously related, if we had the power to replace the radicals  $R$  by *different* groups *without*



thereby producing a distortion of the original molecule  $C(R_1)_4$ . Such a symmetrical arrangement of *different* groups round the central carbon-atom is of course very improbable, although it is not necessarily to be considered as wholly impossible.

§ 15. According to the Van 't Hoff-Le Bel-theory therefore, *the possibility always exists of a chemical substance occurring in two enantiomorphously related isomerides, as soon as a plurivalent asymmetric atom of the kind just described is present in its molecules.*

As already pointed out, this doctrine has proved admirably far reaching: for not only have hundreds of such carbons-compounds



J. H. Van 't Hoff.  
1852—1911



J. A. Le Bel.

been since resolved into their antipodes, but also in the case of other plurivalent atoms than carbon, it has been proved to hold absolutely. Its truth was upheld in the case of the *asymmetric pentavalent nitrogen-atom*, as Le Bel, Kipping, Pope, Wedekind, Aschan, and many others, have demonstrated in a series of admirable investigations <sup>1)</sup>.

<sup>1)</sup> J. A. Le Bel, *Compt. rend. de l'Acad. d. Sc. Paris* **112**. 725. (1891); E. Wedekind, *Zur Stereochemie des fünfwertigen Stickstoffs*, Leipzig, (1899); W. J. Pope and S. J. Peachy, *Journ. Chem. Soc. London* **75**. 1207. (1899);

Pope, Kipping and their collaborators were able to proof the validity of these views also in the case of the *asymmetric tetravalent sulphur-atom*<sup>1)</sup>, of the *asymmetric selenium-atom*<sup>2)</sup>, of the *asymmetric tin-atom*<sup>3)</sup>, while the work of Kipping<sup>4)</sup> on the *asymmetric silicium-atom* has splendidly confirmed the truth of this doctrine in these cases too. Moreover, for the *pentavalent phosphorus-atom*, if asymmetric, the analogous fact was proved by Meisenheimer and Lichtenstadt<sup>5)</sup>, and by Kipping<sup>6)</sup>; so there can be no doubt whatever as to the general correctness of the view that *all* higher-valent ( $v > 3$ ) atoms may eventually reveal the said phenomenon.

As the subject of the application of Van 't Hoff-Le Bel's theory to organic chemistry, and to the numerous particulars and special cases of isomerism in this field, e. g. with unsaturated compounds and the derivatives of trivalent nitrogen, etc., — is too large to be dealt with in detail in this book, the reader must for that purpose be referred to the many text-books on stereochemistry now in use. It need only be remarked that a *final* result as to the arrangement of the radicals round the asymmetric pentavalent nitrogen-atom, could up till now *not* be obtained from the study of the possible isomerides in the case of such compounds as:  $N^V(abcde)$ ,  $N^V(a_2bcd)$ , and  $N^V(a_3bc)$ .<sup>7)</sup> Much work in this field remains yet to be done.

§ 16. The foregoing leaves the impression that the truth of Pasteur's first postulation, namely: the general and constant

79. 828. (1901); W. J. Pope and A. W. Harvey, *Proceed. Chem. Soc. London* 17. 120. (1901); *Proc. Cambr. Phil. Soc.* 12. 466. (1904); H. O. Jones, *Journ. Chem. Soc.* 83. 1400 (1903); E. Wedekind and E. Fröhlich, *Ber. d. d. Chem. Ges.* 38. 1838. 3438. (1905); M. Scholtz, *Ber. d. d. Chem. Ges.* 37. 3627. (1904); 38. 1289. (1905); F. S. Kipping, *Journ. Chem. Soc. London* 83. 873, 918. (1903); O. Aschan, *Zeits. f. phys. Chemie*, 46. 293. (1903); A. W. Harvey, *Journ. Chem. Soc.* 87. 1481. (1905), W. J. Pope and J. Read, *Journ. Chem. Soc. London* 101. 519. (1912).

1) W. J. Pope and S. J. Peachy, *Journ. Chem. Soc.* 77. 1072. (1900); S. Smiles, *ibid.* 77. 1174. (1900).

2) W. J. Pope and A. Neville, *Journ. Chem. Soc.* 81. 1079. 1552. (1902).

3) W. J. Pope and S. J. Peachy, *Proceed. Chem. Soc.* 16. 42, 116. (1900); Cf.: A. Werner, *Lehrbuch der Stereochemie*, p. 316.

4) F. S. Kipping, *Journ. Chem. Soc.* 91. 209, 717. (1907); 93. 457. (1908); 95. 69, 408. (1909).

5) J. Meisenheimer and L. Lichtenstadt, *Ber. d. d. Chem. Ges.* 44. 356. (1911).

6) F. S. Kipping and F. Challenger, *Journ. Chem. Soc. London*, 99. 626. (1911).

7) F. S. Kipping, *Journ. Chem. Soc. London*, 83. 873, 918. (1903).

connection between molecular dissymmetry and optical activity, has been firmly established by experiment; and also, that the doctrine of the so-called "asymmetric plurivalent atoms", as proposed by Van 't Hoff and Le Bel in most cases really gives a sufficient and rational explanation of the significance of this molecular dissymmetry. In general features this is true: nevertheless there remain some difficulties which can best be elucidated if we go somewhat further into the essentials of Van 't Hoff's idea.

Properly speaking, the doctrine of the asymmetric carbon-atom deals with *two* factors at the same time, which are superposed the one upon the other, without it being quite certain that they must necessarily always be mutually connected. For Van 't Hoff's conception not only contains the idea of the *dissymmetrical arrangement* of atoms or radicals in the molecules; but it lays stress also on the *chemical differences* which, according to these views, must necessarily co-exist between the substitutes which are dissymmetrically placed round the asymmetric atom under consideration.

This last view is, however, by no means justified: in the preceding chapters we have often met with geometrical complexes and arrangements in space of *identical* structural units, which nevertheless represented stereometrical *configurations differing from their mirror-images*. It turned out that such arrangements, built up from *identical* units, could yet very well appear in enantiomorphously related forms. The condition of the "dissymmetrical configuration" in Pasteur's meaning of the word, including the possibility of the occurrence of right and left-handed isomerides, is therefore by no means exclusively dependent on a *variety* between the constituting unities of the complex considered. Even if they are *identical*, the molecule as a whole will possibly manifest such a non-superposable symmetry of its configuration.

In the same way we may put the question: can *different* atoms or radicals eventually be arranged in such a way round a plurivalent atom, as to form a higher symmetrical complex *not* differing from its mirror-image? The answer must certainly be that they can: in such a case we should have to imagine that the four different substitutes  $R_1$ ,  $R'$ ,  $R''$ ,  $R'''$  placed round the central atom, notwithstanding their difference in chemical nature, were placed at the corners of a regular tetrahedron or of another symmetrical figure, no appreciable distortion being caused for some reason or other. This arrangement is not very probable, but its possibility cannot

at present be denied, as we do not know anything as to how the chemical forces between the substitutes act, and such a contest of attracting and repulsing forces may be imagined, which would exactly produce the rather strange and certainly very rare arrangement foreseen in this connection.

It will be clear from this that in each of both cases supposed, the plurivalent central atom would be only *partly asymmetric*, if the word is used in the meaning of Van 't Hoff's theory: for in the case first mentioned, the non-superposable arrangement exists, but *not* the contrast in chemical nature of the asymmetrically arranged substitutes; in the second case, the chemical differences between the substitutes, as postulated by Van 't Hoff and Le Bel, are present, but the arrangement of the whole is in this hypothetical molecule such as to make the occurrence of two non-superposable, isomeric molecules impossible here. The last case may be almost accidental, but of the first several instances are now known and have been already sufficiently studied, as we shall soon see. And in this case it has indeed been fully confirmed that the optical activity of the molecule is not so much due to the chemical contrast between the substitutes round the central atom, as to the degree of symmetry, or dissymmetry, of their arrangement in space.

From this it appears necessary in all problems in the domain of stereochemistry, always to find out *what* is the influence of the *one*, and what of the *other* of the two factors considered above?

We must investigate whether in the case of Pasteur's law, the observed properties of the molecule are principally governed by the non-superposable arrangement of the constituent radicals, or by their chemical contrast, or by both causes. Only when we shall have succeeded in separating both these factors out of the fullness of their common manifestations, we can hope to get a clearer insight into the true significance of Pasteur's law, and of the part played by Van 't Hoff-Le Bel's suggestive theory in explaining it <sup>1)</sup>.

§ 17. With respect to the fact that the occurrence of optical antipodes can also take place, only if the arrangement of the atoms be different from its mirror-image, independently of the special circumstance that certain chemical differences of the substitutes are present or not, we can now at once infer that *every chemical molecule must be considered to be resolvable into enantiomorphously*

<sup>1)</sup> F. M. Jaeger, *Proceed. Kon. Akad. v. Wet. Amsterdam*. **17**. 1217. (1915); **18**. 49. (1915); *Chemisch Weekblad*, **14**. p. 706—732. (1917).

*related components, when the stereometrical configuration of its atoms possesses only axial symmetry.*

If however the configuration of the molecule be such that it has either axes of the second order, or one or more planes of symmetry, there is no possibility of antipodes occurring; the case where there exists a symmetry-centre in the chemical molecule is of course also included.

Properly speaking, only the cases where a *single* asymmetric carbon-atom, or more generally: a *single* plurivalent asymmetric atom, is present in a chemical molecule, fall under the simple idea of Van 't Hoff-Le Bel's theory, because only in such cases is the dissymmetry of the molecule really immediately evident, at least, if we disregard for the moment the highly exceptional and very improbable case of an arrangement which will accidentally appear abnormally symmetrical. When however *several* asymmetric atoms in the molecule are present, and especially when we have to deal with so-called *cyclic* compounds, or with such possessing double bonds in their molecules, the symmetry of the stereometrical configuration must be studied carefully, so as to be sure that the conclusions drawn about the eventual occurrence of antipodes are really right. Many erroneous statements on this subject are to be found in works on chemistry; and although the full discussion of this matter cannot be given here, — this being properly more the special subject of text-books on stereochemistry, rather than that of the present volume, — yet it seems desirable to treat some important cases here more in detail, because of the great significance of these views, and for the purpose of illustrating the general applicability of the doctrine of symmetry as developed in the previous chapters, to problems of the kind just mentioned also.

**§ 18.** Before recapitulating these, it is perhaps better first to make a few remarks on the optical activity of carbon-compounds which possess only *one* asymmetric carbon-atom.

The theory of Van 't Hoff and Le Bel has been tested experimentally in a great number of cases, and its correctness has really been fully confirmed.

In all the compounds investigated, the asymmetric carbon-atom was always linked to at least one other carbon-atom; and the question may arise whether the conclusions drawn from that theory will also be valid in cases in which *no* other carbon-atoms whatever are linked directly to the asymmetric one?

Swarts <sup>1)</sup>, who first tried to solve this question, prepared *fluoro-chloro-bromo-acetic acid*:  $\text{CFClBr.COOH}$ , which by means of *strychnine* was resolved into its antipodes, the optical activity of which was measured, but appeared to diminish rather rapidly because of progressing racemisation. On carefully heating both antipodes, carbon-dioxide was split off, and *fluoro-chloro-bromo-methane*:  $\text{CFClBrH}$  resulted. The product obtained appeared however to be quite *inactive*, its constitution evidently involving a great tendency to auto-racemisation.

It was only recently that convincing proof was given of the truth of the theory in cases like this also. Pope and Read <sup>2)</sup> succeeded in resolving *chloro-iodo-methane-sulphonic acid*:  $\text{CHClI}(\text{SO}_3\text{H})$  into its antipodes, and in measuring the optical activity of its *ammonium-salt*:  $(M)_D$  appeared to be about  $44^\circ$  in aqueous solution. In this way full evidence was given that the question put above must be considered as completely proved.

§ 19. Up till now no general rules have been found as to the magnitude of the rotatory power of those compounds which have only one single asymmetric carbon-atom. At first the opinion was, that the greater the chemical difference between the four groups or atoms linked to the asymmetric carbon-atom was, the greater also the rotatory power would appear to be. However all kinds of irregularities and exceptions became gradually known; for instance it proved that the salts of active acids had often just the opposite rotatory power, or a feebler one, than the acids themselves, although the introduction of the metal-atom in place of the hydrogen-atom of the carboxyl-group augmented in many cases the chemical contrast between the four substitutes.

Guye <sup>3)</sup> especially tried to give a rational explanation of this and similar phenomena, by the compelling idea of the *asymmetry-product*. His theory starts with the hypothesis that the degree of molecular dissymmetry depends on the difference in *mass* of the four substitutes linked to the asymmetric carbon-atom. If the masses of the four substitutes be supposed to be concentrated at the corners

<sup>1)</sup> F. Swarts, Bull. de la Soc. Chim. (3). **15**. 1134. (1896); Mém. de l'Acad. roy. de Belgique, **54**. (1895); Bull. de l'Acad. Belg. (3). **31**. 38. (1895).

<sup>2)</sup> W. J. Pope and J. Read, Journ. Chem. Soc. **105**. 811. (1914); Proc. Cambridge Phil. Soc. **17**. 475. (1914).

<sup>3)</sup> Ph. A. Guye, Compt. rend. de l'Ac. d. Sc. Paris **110**. 744. (1890); Thèse, Paris, (1891); Confér. dev. la Soc. Chim. Paris, (1891).

of an irregular tetrahedron, which shall represent in outlines the configuration of the four substitutes round the central asymmetric carbon-atom, then the gravitation-centre of the whole complex will seem to be shifted towards the heaviest substitute, its position being determined with relation to the planes which pass respectively through every edge of the tetrahedron and the middle of the opposite edge. If the distances of this gravitation-centre from the six planes thus obtained be known, its position in space will be absolutely determined. Guye concludes from these reasonings that a substitution in an active molecule always produces a change of algebraic sign of the rotatory power, whenever the gravitation-centre of the new product, in comparison with that of the original molecule, is displaced by the substitution in such a way that it arrives at the opposite side of one of the six planes mentioned above; if after substitution the centre of gravitation remains at the same side of the six planes as it was before, the algebraic sign of the rotation will remain unchanged. If  $d_1, d_2, d_3, \dots, d_6$  be the distances of the gravitation-centre from each of the six planes mentioned above, the product:  $P = d_1 d_2 d_3 d_4 d_5 d_6$  will be, according to Guye's views, a *measure for the dissymmetry of the chemical molecule*<sup>1</sup>). The algebraic sign of the product will change from positive to negative, and conversely, and with it that of the rotatory power of the molecule, when the number of factors out of this group of six which are changed from positive to negative and conversely, happens to be an *odd* one. Indeed, if one of the four substitutes obtain the same mass as one of the others, one of the factors  $d$  becomes *zero*, and therefore so does  $P$  also: i. e. the activity disappears, and experience often confirms this. If instead of the one antipode, the enantiomorphous one be considered, the number of factors  $d$  which change their signs, is always *odd*; thus the activity too changes its sign from positive to negative and conversely<sup>2</sup>).

If  $m_1, m_2, m_3$  and  $m_4$  be the masses of the four substitutes, Guye's formula may be reduced also to the form:

$$P = (m_1 - m_2)(m_1 - m_3)(m_1 - m_4)(m_2 - m_3)(m_2 - m_4)(m_3 - m_4).$$

The same considerations can be used here: thus, if two of the masses become equal,  $P$  becomes *zero*, etc.

<sup>1</sup>) About an application of these views to compounds which contain a pentavalent asymmetric nitrogen-atom, see: M. B. Thomas and H. O. Jones, Journ. Chem. Soc. London, 89. 280. (1906).

<sup>2</sup>) Force more general form of argumentation, cf.: W. Nernst, Theoretische Chemie, (1898). p. 325.

However it is just in this respect that the weak point of Guye's suggestive theory lies: for if the asymmetric carbon-atom be linked to two isomeric radicals  $A$  and  $A'$ , which accidentally possess equal masses, the molecule can yet have optical activity, as has been shown by direct experiments.

Thus Fischer and Flatau <sup>1)</sup> succeeded in performing the fission of *propyl-isopropyl-cyano-acetic acid*:

into its antipodes, and demonstrated that these have a rather large specific rotation ( $11^\circ$ ), notwithstanding the equality of mass of the *propyl*-, and *isopropyl*-groups.

Indeed, the mass-differences of the substitutes appear to have quite a secondary importance for the magnitude of the specific rotatory power of the molecules, as may be seen from the following examples.

Werner <sup>2)</sup> in his masterly investigations on complex inorganic salts exhibiting optical activity, has demonstrated that derivatives of the atoms of trivalent *Co*, *Cr*, *Rho*, *Fe*, etc., which all have the co-ordinative number six, and which belong to the type:  $Me\{(X'')_3\}R_3$ , in which  $X''$  is a bivalent radical or base, can be resolved by suitable means and under favorable circumstances, into two enantiomorphously related antipodes which, although all substitutes  $X''$  are here *equal* and thus have *the same mass*, exhibit an *enormous rotatory power*, surpassing all that has been observed up till now in carbon-compounds. These optically active salts belong to the most interesting and remarkable objects chemistry offers, and their physical properties are so wonderful, that their detailed study will certainly reveal many surprises yet.

*Fig. 163* for example may give some impression of the enormous rotatory power and rotation-*dispersion* of the *tri-ethylenediamine-cobalti*-salts, which may be compared with the dispersion-curve of ordinary *cane-sugar*, represented by the almost straight line beneath <sup>3)</sup>. Often abnormal dispersion-phenomena are observed here

1) E. Fischer and E. Flatau, Ber. d.d. Chem. Ges. 42. 981. (1909).

2) A. Werner, Ber. d.d. Chem. Ges. 45. 121. (1912); 47. 1960, 3093, (1914); etc.

3) F. M. Jaeger, Proceed. Kon. Akad. v. Wet. Amsterdam, Vol. 17. 1231. (1915).



also, e. g. in the case of the complex *tri-oxalates* of *chromium* and *rhodium*<sup>1)</sup>; many other properties moreover, make such dissymmetrical compounds highly promising objects for research.

If we examine more closely the atomistic arrangement of these complex salts, as deduced from Werner's co-ordination-theory, it

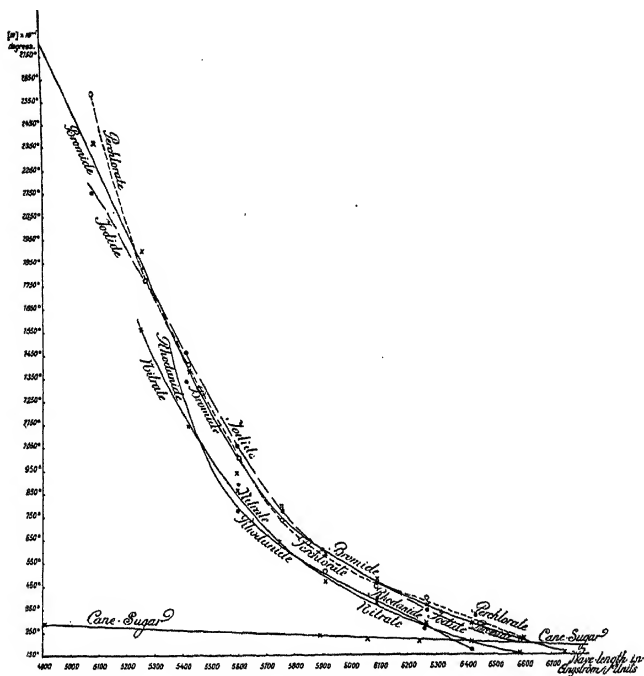


Fig. 163.

Rotation-dispersion of the optically active *Tri-ethylenediamine Cobalt*-salts.

appears that these molecules are by no means unsymmetrical: for instance, the *tri-ethylenediamine-cobalti*-complex has the symmetry represented in the accompanying figures. (fig. 164). It appears that the stereometrical configuration has a ternary axis  $A_3$  and three heteropolar binary axes situated in a plane perpendicular to  $A_3$ .

<sup>1)</sup> F. M. Jaeger, *Proceed. Kon. Akad. v. Wet. Amsterdam*, Vol. 17. 1224. (1915). 19. (Aug.) (1917).

This symmetry is that of the axial group  $D_3$ , and therefore the arrangement must be different from its mirror-image.

Here we have an excellent example of a molecule composed of even *identical* units, which possesses a *rather highly symmetrical configuration*, and which, notwithstanding this, may be obtained in two enantiomorphously related modifications, because its symmetry belongs to the groups which have only symmetry-properties of the *first* order. The enormous rotatory power of these compounds is therefore merely due to the non-superposable arrangement as such,

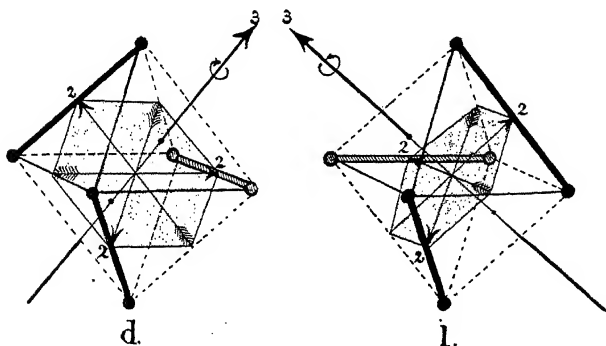


Fig. 164.

The Symmetry of the Ions:  $[\text{Me}(\text{X}'')_3]$ .

and to the special nature of the central metallic atom, *not* however to any chemical contrast between the groups round the plurivalent atom<sup>1)</sup>.

That the special nature of the central metal-atom also takes a predominant part in this, can be seen on comparing the magnitude of the molecular rotation of some analogously composed salts of the metals *Cr* and *Co*:

$$\left\{ \begin{array}{l} \text{Cr}(\text{C}_2\text{O}_4) \\ (\text{Einc})_2 \end{array} \right\} \text{Br}, \quad (M)_D = \text{ca. } 1100^\circ; (M)_C = \text{ca. } 545^\circ$$

$$\left\{ \begin{array}{l} \text{Co}(\text{C}_2\text{O}_4) \\ (\text{Einc})_2 \end{array} \right\} \text{Br}, \quad (M)_D = \text{ca. } 2525^\circ; (M)_C = \text{ca. } 906^\circ,$$

<sup>1)</sup> Cf. W. J. Pope, Presid. Address to the Chem. Section. Brit. Assoc. Rep. (1914): "It must however be insisted, that the observed optical activity is the result of the enantiomorphism of the molecular configuration; the asymmetry of a particular atom is not to be regarded as the cause of the optical activity, but merely as a convenient geometrical sign of molecular enantiomorphism."

the rotation of the *cobalti*-salt being about *double* that of the corresponding *chromi*-salt.

From the following examples <sup>1)</sup>:

$\{Cr(Eine)_3\}I_3$ ,  $M_D = +378^\circ$ ;  $\{Cr(Eine)_3\}(SCN)_3$ ,  $[M]_D = +335^\circ$ .  
 $\{Co(Eine)_3\}I_3$ ,  $M_D = +1072^\circ$ ;  $\{Co(Eine)_3\}(SCN)_3$ ,  $[M]_D = +781^\circ$ .  
 $\{Rh(Eine)_3\}I_3$ ,  $M_D = +329^\circ$ ;  $\{Rh(Eine)_3\}(SCN)_3$ ,  $[M]_D = +335^\circ$ .  
 the remarkable fact is best elucidated that the *Rho*-salts exhibit *about the same rotation* as the *Cr*-salts, although the atomic weight of *rhodium* is about twice that of *chromium*.

The author however cannot agree with the Swiss investigator in the reasonings by which he thinks to have proved that the *algebraic sign* of the rotation in the case of the derivatives of the *tri-ethylene-diamine-rhodium-ion* is also the *opposite* to that of the rotation shown by the *cobalti*-salts of analogous stereometrical configuration.

Werner, (*loco cit.* p. 1229) going on the supposition that salts derived from optically active ions of analogous constitution will combine with the same optically active substance to form compounds which will always show a *relatively comparable degree of solubility* <sup>2)</sup>, has concluded that the *laevogyrate rhodium*-salts and the *dextrogyrate cobalti*-salts which are set free from the *less soluble halogeno-d-tartrates*, must possess the *same configuration in space*. Therefore, according to this author, if in the *tri-ethylenediamine*-complex of the *cobalti*-salts the central *cobalt*-atom be replaced by the *rhodium*-atom, not only the *size* of the specific rotation would be altered, but even *its direction would be reversed*. However Werner does not give any plausible argument to support his starting-point regarding a direct connection between the configuration of the molecules and their solubility. Moreover this view seems to be quite fortuitous, as the solubility of compounds is so highly complicated a constitutive property of matter, that even where rules for homologous compounds apparently universally valid seem to be established, the most unexpected and surprising facts often appear to make them illusory afterwards. The *crystal-form* of the substances, on the contrary, is a property

<sup>1)</sup> A. Werner, Ber. d. d. Chem. Ges. **45**. 1234, 1236. (1912); F. M. Jaeger, Proceed. Kon. Akad. v. Wet. **17**, **18**, **19**; Chem. Weekbl. **14**. 718. (1917).

<sup>2)</sup> As Werner, [Ber. d. d. Chem. Ges. **45**. 1229. (1912)] first suggested, those antipodes, which combine with the same optically active acid or base into the less soluble compound, should always be those of corresponding stereometrical configuration. Therefore, according to this author, the *laevogyrate Rh* should correspond to the *dextrogyrate Co*-salts, and vice versa.

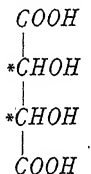
much more directly connected with their *geometrical* character, i. e. with their atomic configuration in space, than is the case with their solubility. If in the *chloro-d-tartrate* of an optically-active *tri-ethylenediamine-cobalti* -ion of definite configuration, the central *Co*-atom under complete preservation of arrangement of the radicals, be replaced by a *Rho*-atom which, according to our investigations, will replace it quite isomorphously, — then it must be obvious that the resultant *rhodium*-salt will appear perfectly isomorphous with the original *chloro-d-tartrate*. Experience however now proves beyond any doubt, that both the less soluble *chloro-d-tartrates* of the *Rho*-, and *Co*-salt possess quite different crystal-forms, the one being triclinicpedial, the other monoclinic, while their parameters do not show the least analogy. Moreover, direct analysis proves that the *chloro-d-tartrate* of the *Co*-salt crystallises with five, that of the *Rho*-salt with four molecules of water, — a fact which is in full agreement with the absence of direct isomorphism between both derivatives too. Both *chloro-d-tartrates* therefore, cannot have an analogous configuration, but they must necessarily possess *antilogous* configurations. This is the simple and true explanation of the fact that the *cobalti*-, and *rhodium*-salts, set free from the less soluble *chloro-d-tartrates*, also show optical rotations of *opposite algebraic signs*. In contradiction to Werner's, our conclusion, therefore, is that the *cobalti*- and *rhodium*-salts with the same direction of rotation possess also the same arrangement of the constituent radicals in space. The influence of replacing a central *cobalt*-atom by a *rhodium*-atom, is therefore manifested only by the change in size of the specific rotation, but not by a change of its direction. As long as no urgent experimental data are available to compel us into another way, it is of importance to construct our plan of the mutual dependence of natural phenomena as simply and transparently as possible; and the conception of the relations between optical activity and configuration of molecules, as explained in the above, seems to us really a simpler and more perspicuous one than that proposed by Werner. For this reason the algebraic signs of the rotation of the *rhodium*-salts are here taken identical with those of the corresponding *cobalti*-salts<sup>1)</sup>.

§ 20. From the foregoing it is evident that for the considerations regarding the eventual possibility of the separation of a chemical

<sup>1)</sup> F. M. Jaeger, *Proceed. Kon. Akad. v. Wet. Amsterdam*, Vol. **19**. (June), (1917); *Chemisch Weekblad*, **14**. 728, (1917).

substance into two enantiomorphously related antipodes exhibiting opposite rotatory power, the question as to the special stereometrical configuration must in each case be brought to the fore. If the conception of Van 't Hoff and Le Bel as to the direction of the four carbon-valencies be adopted, and keeping that in mind, the stereometrical "model" of the molecule be constructed, we have only to make sure that the configuration thus obtained has *no* axis of the *second* order, nor any symmetry-plane, nor a centre of symmetry<sup>1)</sup>. If this be done, the compound will be such as to be resolved into enantiomorphous isomerides. But if one of the symmetry-properties of the second order mentioned be found in the model, the substance will *not* be resolvable into two enantiomorphously related isomerides, not even if there be eventually several asymmetric carbon-atoms present in it. A few instances may be exemplified here to make this clear.

§ 21. The oldest known example of a compound which cannot be resolved into enantiomorphous isomerides although it possesses several asymmetric carbon-atoms, is *meso-tartaric acid*:

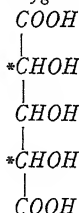


Evidently the one half of the molecule is here the mirror-image of the other half; or what is the same thing: the stereometrical configuration of atoms has here a *plane of symmetry*, and therefore it *cannot* differ from its mirror-image. Formerly this was explained by saying that the rotatory effect of the one half of the molecule was counterbalanced by that of the other half, and such molecules were therefore said to be inactive and non-resolvable by *internal compensation*. The explanation given here is however better, because it does not introduce any superfluous hypothesis, but elucidates

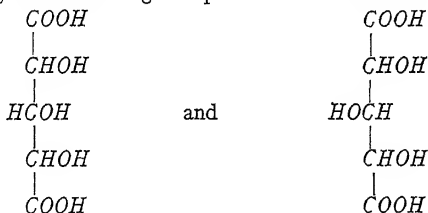
1) The "plane of indirect symmetry", as mentioned by Ladenburg, and by Groth in the discussion of the impossibility to resolve certain *diketo-piperazines* into antipodes, corresponds to no other operation than *inversion*. Such molecules cannot be separated in enantiomorphous modifications, because they have an *inversion-centre*, which is equivalent to a binary-axis of the *second* order; they are therefore congruent with their mirror-images. It is quite superfluous to introduce here any new name.

the fact merely as a direct consequence of the general doctrine of symmetry. It simply states that no enantiomorphism of stereometrical arrangement can ever occur, when the configuration of atoms as a whole shows any symmetry-element of the second order<sup>1)</sup>.

The same is true with *trioxylglutaric acid*:

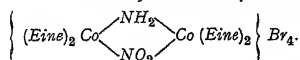


although a little modification of what was said above will be necessary here because the *middle* one of the three carbon-atoms is in a somewhat peculiar position relative to both the others. For although the carbon-atom in the midst of the molecule is *not* asymmetric, it has however an influence on the number of possible isomerides, as a second inactive and non-resolvable isomeride may occur here, which also is *inactive* "by internal compensation", but which differs from the first by the interchange in space of the substitutes *H* and *OH*:



Of course, we shall therefore have, as in the cases of the *meso-tartaric acid* and *tartaric acids* mentioned above, not only two active and one inactive form besides the *racemic* compound, but two active and two inactive isomerides. A carbon-atom as found here in the midst of the molecule of *trioxylglutaric acid*, is called a *pseudo-asymmetric* carbon-atom.

<sup>1)</sup> A case similar to that of *meso-tartaric acid*, etc., has also been studied by Werner in the case of *tetra-ethylenediamine-μ-amino-nitro-dicobalti-bromide*:



Indeed, besides the *d*-, *l*-, and *rac.* compound, an *inactive*, *non-resolvable* isomeride could be obtained; cf.: Ber. d. d. Chem. Ges. 46. 3674. (1913).

As to the *number* of isomerides which can be expected when the number of asymmetric and pseudo-asymmetric carbon-atoms in the molecule is known, the following data may suffice.

If  $n$  be the number of true asymmetric carbon-atoms in the molecule,  $N_a$  the number of the possible optically active isomerides,  $N_i$  that of the possible inactive and non-resolvable isomerides, and  $N_r$  the number of racemic compounds, we have in the various cases the following relations:

a) If no reduction of the number of isomerides occurs, neither by "internal compensation", nor by the presence of a pseudo-asymmetric carbon-atom in the molecule, then generally:

$$N_a = 2^n, \text{ and } N_r = \frac{1}{2} N_a = \frac{1}{2} \cdot 2^n, \text{ while } N_i = 0 \text{ here.}$$

b) If internal compensation occurs, *without* the influence of a pseudo-asymmetric carbon-atom, then:

$$N_a = 2^{n-1}, N_r = \frac{1}{2} \cdot 2^{n-1}, \text{ and } N_i = 2^{\frac{n}{2}-1}.$$

c) If there be a pseudo-asymmetric carbon-atom, these numbers become:

$$N_a = 2^{n-1} - 2^{\frac{n-1}{2}}; N_r = \frac{1}{2} (2^{n-1} - 2^{\frac{n-1}{2}}); \text{ and } N_i = 2^{\frac{n-1}{2}}.$$

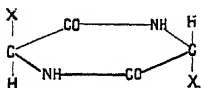
§ 22. In the case considered here, the impossibility of the fission of the *meso-tartaric acid* and of the two inactive *trioxylglutaric acids* was an immediate consequence of the existence of a symmetry-plane in their atomistic arrangement. The same however must occur if the arrangement have a *mirror-axis* or a *symmetry-centre* among its symmetry-elements. Such cases can occur, as soon as asymmetric carbon-atoms are units of a *cycle* of atoms. A few selected instances may further explain this.

If there be only a single asymmetric carbon-atom in the ring, the influence produced by that atom is in principal features the same as that in open-chain compounds with a single asymmetric atom. In such cases the plane of the ring can of course never be a symmetry-plane of the molecule, and the number of isomerides is *two*, not counting the *racemic* compound. If however there be *two* or *more* asymmetric carbon-atoms, more detailed examination is necessary.

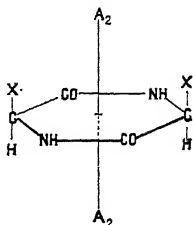
Ladenburg<sup>1)</sup> drew attention to the fact that the *trans*-modification of the *diketo-piperazines* (*A*), is *not* resolvable into enantiomorphous isomerides. He, and later Groth<sup>1)</sup>, explained this by indi-

<sup>1)</sup> A. Ladenburg, Ber. d. d. Chem. Ges. 28. 1955, 3104. (1895); P. Groth, ibid. 28. 2510. (1895). Cf. the note on page 244.

cating the existence of a "plane of indirect symmetry"; however the symmetry-operation corresponding to it is nothing but an *inversion*, as has already been indicated. The *trans*-form of 1-4-diketo-2-5-dimethyl-piperazine (*trans*-alanyl-anhydride) has an inversion-centre, and has thus the symmetry of the group *I*. The *cis*-form (*B*) however evidently has a *single polar binary axis*  $A_2$ , perpendicular to the plane of the ring; it possesses therefore *only axial symmetry* ( $C_2$ ):



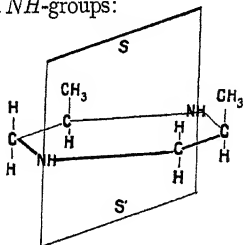
A.



B.

and accordingly its arrangement must differ from its mirror-image. Indeed, Fischer and Raske<sup>1)</sup> have shown that these compounds exist in *four* isomeric forms: a laevo- and a dextrogyrate isomeride, and a racemic compound, all three corresponding to the *cis*-form, and one inactive *trans*-isomeride which can not be resolved into optically active antipodes.

Pope and Read<sup>2)</sup> tried to demonstrate the same with 2-5-dimethyl-piperazine itself, without result however. Afterwards they made it probable<sup>3)</sup> that here *not* the 2-5-, but the 2-6-*cis*-derivative was treated, which cannot be split up, because it has a single plane of symmetry perpendicular to the plane of the ring, and passing through both *NH*-groups:



1) E. Fischer and K. Raske, Ber. d. d. Chem. Ges. **39**, 467, 3981. (1906).

2) W. J. Pope and J. Read, Journ. Chem. Soc. **101**, 2325. (1912); C. Stoehr and collaborators, Journ. f. prakt. Chemie (2). **55**, 49—77. (1897).

3) W. J. Pope and J. Read, Journ. Chem. Soc. London **105**, 219. (1914).



The molecule thus possesses the symmetry of the group of the second order  $S$ .

Another instance of a similar kind is found in the case of *methane*<sup>1)</sup>, and of *tetra-methylene*-derivatives of special configuration. Let us imagine molecules such as:

$[CH.C(abc)]_2$  or  $C[d-Cabc]_2(l-C(abc)_2]$   
which are represented by the models in *fig. 165* and *166*:

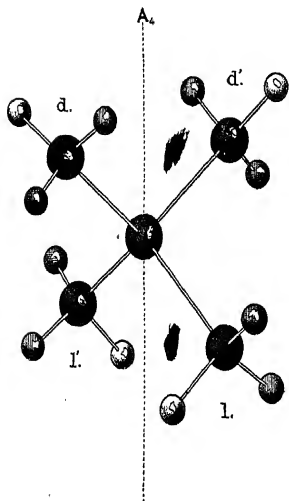


Fig. 165.

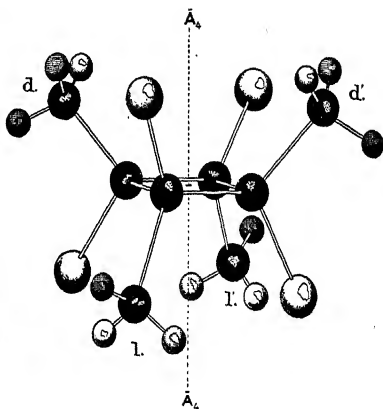


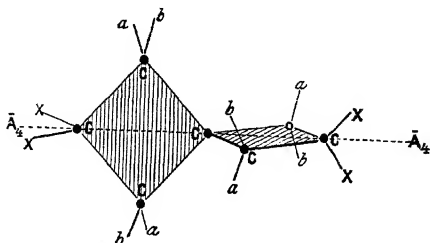
Fig. 166.

Such molecules possess no less than *four* or *eight* asymmetric carbon-atoms, and also they have neither an inversion-centre nor a plane of symmetry. Notwithstanding this, these compounds can *never* be resolved into optically active antipodes, because both molecules have *a single quaternary mirror-axis*  $\bar{A}_4$  perpendicular to the plane of the ring in the second, and placed vertically in the first formula. Having thus a symmetry-element of the second order in their atomistic arrangement, the configuration of the molecules must be congruent with its mirror-image (group  $\bar{C}_4$ ), and therefore no fission of the proposed kind can be possible.<sup>2)</sup>

1) G. Hartwall, Dissertation, Helsingfors, (1904).

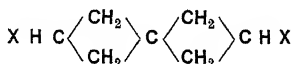
2) The groups  $(Cabc)$  are unsymmetrical, and thus are *different* from their mirror-images. To avoid confusion, it is better therefore to discriminate them pairwise by the prefixes *d*-, and *l*-; just because *d*-( $Cabc$ ) and *l*-( $Cabc$ ) are non-

We find an analogous case of the presence of such a mirror-axis in the molecule, if we consider the following configuration:



The symmetry is here  $\bar{C}_4$ ; but if the two groups  $X$  linked at the same carbon-atom be made *different* (e.g.  $X$  and  $H$ ), the mirror-axis  $\bar{A}_4$  will disappear, and the molecule, being now completely asymmetrical, may be resolved eventually into optically active antipodes.

Even if the molecule had simply the formula:



the possibility of a separation into antipodes will be present.<sup>1)</sup>

If in the cases of *fig. 165* and *166*, one or two of the asymmetric carbon-atoms are changed into higher symmetrical radicals, the molecules obtained will be resolvable, notwithstanding the fact that the number of asymmetric carbon-atoms is now diminished.

§ 23. Should there be also a pseudo-asymmetric carbon-atom in the ring, then the number of optically inactive, non-resolvable isomerides will be increased, exactly as in the case of the open-chain-derivatives formerly discussed.

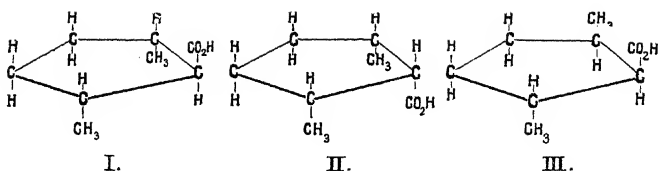
Thus Wislicenus succeeded in obtaining *three* isomerides of *2-5-dimethyl-cyclopentane-1-carboxylic acids*.<sup>2)</sup> Two of them are *cis-cis*-forms (*I* and *II*; mpts:  $30^\circ C$ , resp.  $77^\circ C$ ), and as each of them has the symmetry of the group  $S$ , they *cannot* be resolved into optically active antipodes. That there are *two* of these "internally compensated" isomerides, is explained by the fact that the carbon-

superposable, the molecule has *not* the symmetry  $D_2$ , as perhaps would appear at superficial examination, but that of group  $\bar{C}_4$ , as already mentioned.

The conclusion of E. Mohr, *Journ. f. prakt. Chem.* (2). **68**. 378. (1903), is erroneous in this respect.

1) O. Aschan, *Ber. d. d. Chem. Ges.* **35**. 3396. (1902).

2) J. Wislicenus, *Ber. d. d. Chem. Ges.* **34**. 2572. (1901).



atom to which the group  $COOH$  is linked, is a pseudo-asymmetric one, while both the neighbouring carbon-atoms are really asymmetric.

The third isomeride (III mpt:  $50^{\circ}C$ ) is a *cis-trans*-form; it must represent a *racemic* compound, because its configuration is wholly asymmetrical (group *A*), and under favorable circumstances it must therefore be possible to resolve it into two enantiomorphously related components. Up till now this fission has however not yet been performed.

In this connection the investigations of Von Baeyer<sup>1)</sup> and Perkin<sup>2)</sup> on the *hexa-hydro-phtalic*-, *-isophtalic*-, and *-terephthalic*-acids may be mentioned here. While both (*cis*-, and *trans*-)-*hexa-hydro-terephthalic* acids have the symmetry *S*, and thus are *not* *resolvable* into optically active antipodes, while the same is the case with the *cis-isomerides* of the corresponding *phtalic*-, and *-isophtalic*-acids, the *trans-hexa-hydro-phtalic*-, and the corresponding *hexa-hydro-isophtalic* acids have however the axial symmetry of the group  $C_2$ . In accordance with this, Werner and Conrad<sup>3)</sup> succeeded in resolving the *trans-hexa-hydro-phtalic* acid by means of its *quinine*-salt, and measured the optical rotation of both antipodes.

Here the fission of *trimethylene-dicarboxylic* acid by Buchner and Von der Heide<sup>4)</sup>, and that of the corresponding *tricarboxylic* acid, may again be mentioned, as being also in full accordance with the theoretical predictions.

§ 24. Again another remarkable case is found in the *inosites*<sup>5)</sup> which have the composition:  $C_6H_6(OH)_6$ , and which must be considered to be *hexa-hydroxy-hexa-hydro-benzenes*. Besides a *racemic*

<sup>1)</sup> A. Von Baeyer, Ann. der Chemie **245**. 103. (1888); **251**. 258. (1889); **258**. 1, 145. (1890).

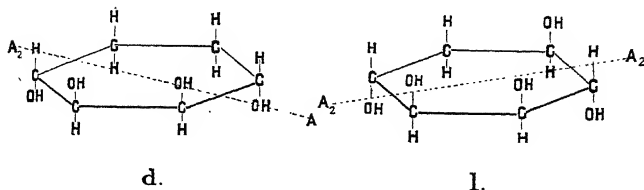
<sup>2)</sup> W. H. Perkin Jr., Journ. Chem. Soc. London **59**. 798. (1891).

<sup>3)</sup> A. Werner and H. E. Conrad, Ber. d.d. Chem. Ges. **32**. 3046. (1899).

<sup>4)</sup> E. Buchner and R. Von der Heide, Ber. d.d. Chem. Ges. **38**. 3112. (1905).

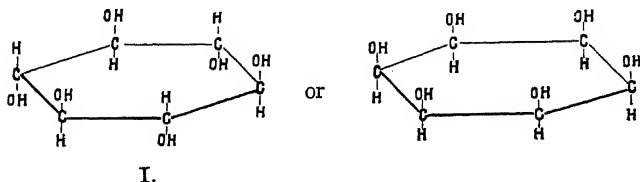
<sup>5)</sup> L. Maquenne, Ann. de Chim. et Phys. (6). **29**. 271. (1893); G. Tanret, Compt. rend. de l'Acad. des Sc. Paris, **109**. 908 (1899).

substance which, according, to Wyrouboff<sup>1)</sup>, crystallises in the holohedral class of the monoclinic system, two optical antipodes:



are known, which crystallise ( $+2H_2O$ ) in the rhombic system, although no hemihedral forms could hitherto be obtained. The molecule of this cyclic compound does not possess, properly speaking, an asymmetric carbon-atom at all, at least not in the sense of Van 't Hoff's and Le Bel's theory. The whole configuration however is such that there is only a *single binary axis of the first order*, the direction of which is indicated in the formula by a dotted line. The symmetry of both molecules is therefore that of the cyclic group  $C_2$ ; the atomistic arrangement, having thus only *axial* symmetry, must be *different* from its mirror-image, and the occurrence of the dextro- and laevogyrotory forms of *inosite* is in this way easily explained, notwithstanding the fact, mentioned above, that *no* true asymmetric carbon-atoms are really present.

Of course optically *inactive*, *non-resolvable* modifications will be possible too in the case of the *inosites*. If the substitutes be placed as follows for instance:

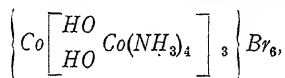


the symmetry of these molecules is a rather high one: in a compound of formula *I*, there is a homopolar trigonal axis perpendicular to the plane of the ring, three homopolar binary axes (including  $60^\circ$ ) in the plane of the ring, and three vertical planes of symmetry passing through the trigonal axis and bisecting the angle between two suc-

<sup>1)</sup> G. Wyrouboff, Bull. de la Soc. Miner. 25. 169. (1902).



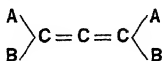
the purpose of giving full evidence that *not* the presence or absence of an asymmetric carbon-atom in the chemical molecules, but rather the special circumstance according to which the atomistic configuration of the molecule as a whole has only *axial* symmetry or not, is a predominant one for answering the question whether the molecule may be considered as resolvable into optically active components or not. As a full proof that even the existence of *no* carbon-atom whatever is necessary for this, we will mention here Werner's *dodecamine-hexol-tetra-cobalti-bromide*:<sup>1)</sup>



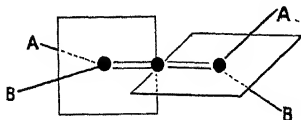
in which the complex:  $\left[ \text{Co} \begin{bmatrix} (\text{OH})_3 \\ (\text{NH}_2)_4 \end{bmatrix} \right]$  evidently plays the same rôle as the *tri-ethylenediamine*-molecule does in the *luteo*-salts mentioned previously. The molecular rotatory power of the active components of this substance amounts to a value of about 47600°; its rotation-dispersion is, moreover, remarkably abnormal.

§ 25. In this respect some other examples are of interest, which are related to cases where *double bonds* between carbon-atoms form part of the peculiarities of the molecules, or where a single carbon-atom is common to two different rings.

A case of this kind was already mentioned by Van 't Hoff, namely in carbon-derivatives of the following kind:



Indeed, a closer examination of the stereometrical model of this molecule will clearly show, that it is completely asymmetrical:

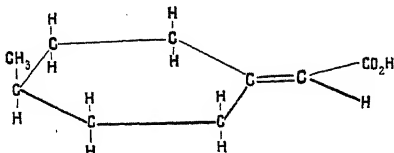


Therefore its configuration must be different from its mirror-image, although no true asymmetric carbon-atoms are present here. Of the special case that a carbon-atom is the connection between two rings, examples have been given already on page 249.

<sup>1)</sup> A. Werner, Ber. d. d. Chem. Ges. 47. 3087. (1914).

Especially in cyclic compounds, the presence of such double bonds can be of interest for the question of the resolvability of the molecule into optically active antipodes.

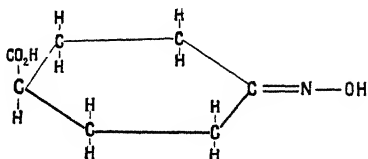
Pope, Perkin and Wallach <sup>1)</sup> prepared and studied the *r*-methyl-cyclohexylidene-4-acetic acid:



This molecule has no symmetry at all, and indeed it appeared to be resolvable into optical antipodes by the aid of *brucine*.

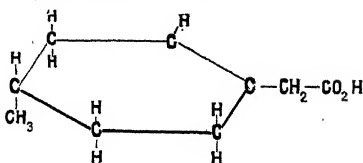
The *dibromo*-addition compounds preserved their activity also, and the same was found for the corresponding *hexanes*. The  $\beta$ -*dextro*-acid could be obtained in tetragonal crystals, measured by Halli-  
mond, but these did not exhibit any trace of hemihedris-  
m.

A case similar to this, is that of *4-oximino-cyclohexane-carboxylic acid*:



which was prepared by Kay and Perkin <sup>2)</sup>, and which was first split up, by means of *morphine*, by Mills and Bain <sup>3)</sup>.

Somewhat different, — because one of the carbon-atoms may be concerned as asymmetrical, — is the case of the fission of the acid:



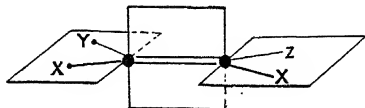
<sup>1)</sup> W. J. Pope, W. H. Perkin Jr., and O. Wallach, Journ. Chem. Soc. London, **95**. 1789. (1909); W. J. Pope and W. H. Perkin Jr., Journ. Chem. Soc. **99**. 1510. (1911); A. E. Everest, Chem. News, **100**, 295. (1909); J. E. Marsh, Proceed. Chem. Soc. **27**. 317. (1911); P. F. Frankland, Journ. Chem. Soc. London **101**. 654. (1912).

<sup>2)</sup> F. W. Kay and W. H. Perkin Jr., Journ. Chem. Soc. **89**. 1640. (1907).

<sup>3)</sup> W. H. Mills and A. M. Bain, Journ. Chem. Soc. **97**. 1866. (1910).

which melts at  $41^{\circ}\text{C}$ ., and was separated by Marckwald and Meth<sup>1)</sup> by means of the acid *cinchonine*-salts.

Some remarks may be made in this connection on the isomerism which, according to some investigators, would occur in *ethylene*-compounds of a constitution like:



In general such *ethylene*-compounds are supposed to be symmetrical with respect to the plane passing through both the double-bond carbon-atoms and all substitutes *X*, *Y*, *Z*, etc.; the study of a great number of *ethylene*-derivatives seems really to have confirmed this view.

However Erlenmeyer Jr. pointed out, that in the cases mentioned above, and especially in that of the isomeric, *cinnamic*, *allo-cinnamic*, and *iso-cinnamic acids*<sup>2)</sup>, an isomerism should be possible, which occasionally should create the possibility of resolving the compound into optically active isomerides. It may be that a special nature of the substitutes *X*, *Y*, and *Z* can be the cause of such an exception of the rule that *ethylene*-derivatives have generally a plan-symmetrical configuration. In any case, the problem although of high interest with respect to our views of the stereometrical arrangement of the atoms in carbon-derivatives in general, has not yet been settled; and it is to be hoped that a new and exhaustive investigation of this evidently very difficult matter will be started within the immediate future, which will definitely show whether we have to give up our present views about the symmetry of such *ethylene*-derivatives.

1) W. Marckwald and R. Meth, Ber. d. d. Chem. Ges. **39**. 1175. (1906).

2) E. Erlenmeyer Jr. Ber. d. d. Chem. Ges. **36**. 2340. (1903); **38**. 2562, 3496. (1905); **39**. 788, 1570. (1906); E. Erlenmeyer Jr., C. Barkow, and O. Herz, Ber. d. d. Chem. Ges. **40**. 653. (1907); E. Erlenmeyer Jr. and A. Arnold, Ann. der Chemie **337**. 329. (1904). Cf. also: C. Liebermann and B. Halvorsen, Ber. d. d. Chem. Ges. **36**. 176. (1903); W. Marckwald and R. Meth, Ber. d. d. Chem. Ges. **39**. 1176, 1966, 2598. (1906); E. Billmann, Ber. d. d. Chem. Ges. **42**. 182, 1443. (1909); **43**. 568. (1910); **44**. 3152. (1911); E. Erlenmeyer Jr. and G. Hilgendorff, Biochem. Zeits. **74**. 137. (1916); **77**. 55. (1916).



The agreement, in by far the biggest number of cases, of theory and experience may be considered as an argument that the representation of molecules by our stereometrical formulae, as proposed by and derived from the original hypothesis of Van 't Hoff and Le Bel, allow as to give a fairly exact account of the most fundamental geometrical properties of such carbon-derivatives. In this respect these formulae may be conjectured as something more than mere outlines, and as really corresponding in at least the most salient features to the true configuration of the atoms in space.

§ 26. After these considerations we may now proceed to the second part of Pasteur's law, connecting the molecular dissymmetry with the appearance of enantiomorphous, hemihedral crystal-forms of the two isomerides, and examine more closely the truth of this conclusion too.

Since Pasteur discovered the occurrence of such enantiomorphously related, hemihedral crystal-forms in the case of both *tartaric acids*, and since he confirmed his original view by the study of a great number of their crystallised derivatives, the question as to the necessary mutual dependence of both phenomena has been discussed several times by different authors.

While there seemed to be no justifiable doubt about the validity of Pasteur's view that molecular dissymmetry is always the cause of optical activity in the sense employed in the foregoing, serious doubt has arisen in later times as to the correctness of Pasteur's conclusion that molecular dissymmetry is necessarily connected with the occurrence of enantiomorphous hemihedral crystal-forms.

The reason of this is obvious. In fact, optical activity is a property existing also in the amorphous state, in solution and in molten masses. It is therefore a property which is directly and intimately connected with the individuality of the single molecule and its particular stereometrical configuration. The crystal-form however is one of the *many* ways in which the symmetrical and periodical arrangement of the crystal-molecules, or at least, of the crystal-units, — manifests itself.

It may be, — and more recent experience seems to support this view, — that the crystal-molecules are identical with the chemical molecules; or even that the conception of a single molecule in crystals no longer holds. But also if this were true, the crystalline form, while depending on the rather complicated arrangement of these crystallographical units, is properly only a *second-hand* pheno-

menon with respect to the inter-atomistic forces which determine the stereometrical configuration of the atoms in the molecule. There are many substances known, which crystallise in well-developed hemihedral forms differing from their mirror-images, but which do not exhibit any rotatory effect in solution or in the liquid state: *sodium-chlorate*, rhombic *magnesium-sulphate*, etc., are well-known instances of this. Why should not the reverse eventually be possible?

Then, there seemed to be a number of apparent exceptions to Pasteur's law, which gradually amounted to a considerable group.

Becke<sup>1)</sup> in 1899 gave a review of about *seventy* cases of optically active substances, *not* exhibiting hemihedral crystal-line forms.

However, in his opinion Pasteur's theory must be still adopted, because there are a much greater number of valid cases, and because the absolute proof of the presence or absence of hemihedrism in many crystallographical researches was or could not be given by the rudimentary development of the crystals, etc. Of course, the first argument is of no significance, where just the special question is put, whether the connection of both phenomena be a *necessary* one?

With respect to the absence of rotatory power in many hexagonal and tetragonal crystals of these optically active substances, he also agrees with the explanation of this given by Mallard<sup>2)</sup> and Wyruboff<sup>3)</sup>, who, from their observations of crystals exhibiting rotatory power, had already concluded that all these crystals were really pseudosymmetrical intercalations, and warned in 1894 against the dogmatic view that an obligatory connection between optical activity and hemihedrism should exist. In 1896 and 1897 Walden<sup>4)</sup> again drew attention to the fact that the number of cases in which a rotatory effect in solution was *not* combined with the occurrence of hemihedral crystal-forms, increased more and more, their number gradually approaching that of the cases in which such hemihedrism was concisely determined.

He is therefore convinced that optical activity in solution or

1) F. Becke, *Tscherm. Min. u. Petr. Mitth.* **10.** 464. (1899); **12.** 256. (1891).

2) E. Mallard, *Traité de Cristallographique II.* p. 330. (1884).

3) G. Wyruboff, *Ann. de Chim. et Phys. (6).* **8.** 416. (1886); **(7).** **1.** 10. (1894); A. Descloizeaux, *Ann. des Mines (5).* **14.** 18.

4) P. Walden, *Ber. d. d. Chem. Ges.* **29.** 1692. (1896); **30.** 98. (1897).

in the liquid state in general, and the hemihedrism of the crystalline forms are *phenomena of a different order*, which have *no* direct causal relation, although they often appear combined and parallel to each other.

On the other hand, Traube<sup>1)</sup> brought forward that the exceptions mentioned by Walden are undoubtedly partially explained by the fact that the corresponding crystallographical data are very incomplete and rudimentary; the cause of this being, that the most suitable circumstances were not found for the development of hemihedral faces in the crystals, or that the investigation was only applied to the external form, without the use of other physical methods of research, as: pyro-electrical observations, corrosion-figures, etc. He emphasizes the fact that only then a convincing proof of the incorrectness of Pasteur's conclusion could be given, if the apparently holohedral crystal-form of an optically active compound really showed corrosion-figures agreeing with holohedral, but not with hemihedral symmetry; this demonstration was, however, not given at that time, because in all cases in which apparently holohedral crystal-forms were mentioned, no corrosion-figures could be obtained suitable for the purpose.

§ 27. Experience has since shown that really hemihedrism could be found in a large number of cases, even in many of those formerly looked upon as exceptions. It is a well-known fact that hemihedral crystalline substances under special circumstances will show the development of hemihedral faces, which will remain latent under other circumstances of crystallisation. *Calcium-bimalate*-crystals ordinarily do *not* show hemihedral faces; but if some free nitric acid be added to the saturated solution, they then appear constantly. According to Pasteur<sup>2)</sup> also the *ammonium*-salt, if crystallised from pure water, does not exhibit hemihedral faces; however these re-appear if the substance be previously melted and then recrystallised from the same solvent. Indeed, very minute amounts of impurities or other substances purposely added to the solutions, can influence to a rather high degree this tendency towards the manifestation of hemihedral faces in such crystals.

Although many examples given by Walden have thus lost their importance as arguments in this principal question however

1) H. Traube, Ber. d. d. Chem. Ges. 29. 2446. (1896); 30. 288. (1897).

2) L. Pasteur, Jahresber. f. Chemie (1852), p. 176; (1853), p. 410.

the problem can by no means be considered to be as yet finally settled.

In a crystallographical investigation of an optically active ketone, *lupeon*:  $C_{31}H_{48}O$  (mpt:  $170^{\circ} C.$ ), prepared in Van Romburgh's laboratory by Cohen, the present author<sup>1)</sup> found a substance which crystallises readily from *acetone* in very beautiful, apparently holohedral rhombic crystals (*fig. 167*). The corrosion-figures obtained on the facets of the prism, showed undeniably the existence of a *horizontal* plane of symmetry, and they were, moreover, situated on adjacent prism-faces in such a way that the existence of two vertical planes of symmetry in the crystals could not be doubted. The corrosion-figures were therefore in full agreement with the apparently holohedral symmetry of the crystals, as inferred from their geometrical form. Groth points<sup>2)</sup> to the desirability of confirming this result by etching two adjacent pyramid-facets. In any case, if hemihedrism be supposed here too, it appears to be so feebly expressed that *no* convincing proof of its existence could hitherto be given; the optical rotation in *chloroform*-solution however amounts here to:  $[\alpha]_D = +63,1$ . This rather great rotation surely bears no proportion to the imperceptible degree of hemihedral development.

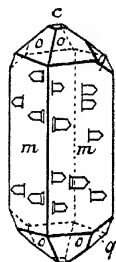


Fig. 167.  
Crystal-form and  
corrosion-figures  
of *Lupeon*.

In an analogous way it was found<sup>3)</sup> that *cholestenon*:  $C_{27}H_{44}O$ , (mpt:  $78^{\circ} C.$ ), prepared by Windaus, crystallises from *ethylacetate* in every case in the prismatic class of the monoclinic system. Here also there can be no doubt about the holohedrism of the crystal-form. It is possible that in molecules of such a magnitude the influence of the asymmetric carbon-atom is almost effaced, and that therefore its presence is by no means revealed in the crystalline form of the compound.

§ 28. With respect to the manifestation of hemihedrism, the question may be asked whether the two factors differentiated in

1) F. M. Jaeger, Zeits. f. Kryst. u. Miner. **44**, 568. (1908); Cf. N. H. Cohen, Rec. de Trav. d. Chim. d. Pays-Bas. **28**, 368. (1909).

2) P. Groth, Chemische Krystallographie *III* p. 526. (1910).

3) F. M. Jaeger, Groth's Chem. Krystall. *III*, 536. (1910); A. Windaus, Ber. d. d. Chem. Ges. **39**, 2008. (1906).

the above, namely: the influence of the stereometrical arrangement on the one side, and that of the chemical inequality of the substitutes on the other side, have not a very different importance in causing the occurrence of crystallographical hemihedrism and that of optical activity?

Now the study of compounds which contain partially asymmetric atoms (p. 235) might give some insight into the question.

Investigations were therefore made into the optical and crystallographical properties of the salts of the trivalent *tri-ethylene-diamine-cobalt-ion*:  $\{Co(Eine)_3\}^{++}$ , first prepared and studied by Werner. Here indeed all substituents round the central Co-atom are *identical*: thus it will be only the influence of the *non-superposable* configuration, that would be expressed in the properties of the derivatives. Therefore we get rid of the influence which is in all these cases combined with the differences between the substitutes, as we have already explained in dealing with the rotatory power of these substances.

Notwithstanding the enormous rotation these optically active salts exhibit, it was now found<sup>1)</sup> that, although in some cases enantiomorphism was really manifested, this was however reduced in several instances to an undetectably feeble degree.

The *d*- and *l*-bromides:  $\{Co(Eine)_3\}Br_3 + 2H_2O$ , did *not* show under any circumstances of crystallisation, the slightest indication of hemihedrism; while in the case of the *iodides*:  $\{Co(Eine)_3\}I_3 + H_2O$ , and of the *rhodanides*:  $\{Co(Eine)_3\}(SCN)_3$ , even the corrosion-figures obtained were in full accordance with holohedral symmetry, instead of being a proof of hemihedrism. If enantiomorphism be present here, it is evidently manifested to such an extremely slight degree that it is not detectable by any crystallographical method at hand.

From this it appears evident that in this case there is surely *no* rational proportion present between the enormous optical activity of the molecules on the one hand, and the undetectable hemihedrism on the other. The cause of this can only be the *equality* of the dissymmetrically arranged substitutes:  $[C_2H_4(NH_2)_2]$ .

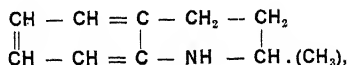
From this it becomes highly probable that, *while the optical*

<sup>1)</sup> F. M. Jaeger, *Proceed. Kon. Akad. v. Wet. Amsterdam*. Vol. **18**. 52, 56, 63, 65, 67. (1915); *Zeits. f. Kryst. u. Miner.* **55**. 209. (1915); *Chemisch Weekblad* **14**. 718—727. (1917).



binary axis of the *second* order in the case of the optically inactive crystals. The hemihedrism of the optically active forms is notwithstanding the enormous rotatory power, here only betrayed by the occurrence of a trigonal bipyramid; not even a single "trapezohedral" facet was ever met with in these salts.

Pope and Peachy<sup>1)</sup> have studied the crystal-forms of the right- and left-handed components of *tetrahydroquinaldine-hydrochloride*:  $C_{10}H_{13}N$ ,  $HCl + H_2O$ ; although the molecular rotation for sodium-light in alcoholic solution was almost  $141^\circ$ , in aqueous solution  $122^\circ$ , the crystals of both antipodes (rhombic) not only showed no trace of hemihedrism, but the corrosion-figures on (001), obtained by means of alcohol + water, were in full agreement with *holohedral* symmetry. If however in the molecule:



whose molecular rotation for sodium-light was about  $85^\circ$  at  $20^\circ \text{C.}$ , the hydrogen-atom of the *NH*-group were substituted by a *benzoyl*-radical, the rotation gets the opposite algebraic sign and is simultaneously increased enormously, its value being now  $814^\circ$ ; and at the same time the hemihedrism of the crystalline forms now appears clearly manifested.

From these data it appears that the connection between molecular dissymmetry and crystallographical hemihedrism, as supposed by Pasteur, may be hidden in many cases to such an extent, that it may be doubtful as to whether it be present in such cases at all. Surely in most cases a parallelism between both phenomena is present: where the dissymmetry of the molecule is betrayed by the rotatory power of the molecules, there is exhibited in most cases also a non-superposable hemihedrism of the crystalline forms. But this need not always be the case. The greater the chemical contrast between the substitutes round the asymmetric atom present in the molecule is, the greater chance there will evidently be, that crystallographical hemihedrism will appear to accompany the rotatory power of the substance. For the magnitude of the rotatory power of the molecule, this chemical contrast between the substitutes is only of secondary significance: here it is the non-superposable stereometrical arrangement and the

special nature of the plurivalent central-atom in the first place, which are the preponderant conditions. In this way we get a little more insight into the mechanism of optical activity and its dependence on molecular configuration, as the beginning of a fuller understanding of the relation between Pasteur's law and Van 't Hoff-le Bell's ingenious theory<sup>1)</sup>.

§ 29. The above remarks bring to the fore another general question regarding optical activity and non-superposable hemihedrism. It is a well-known fact that there are a number of substances which crystallise in undeniably enantiomorphous crystal-forms, but which behave quite differently with respect to polarised light.

According to Pope<sup>2)</sup> three classes of substances may be distinguished, as:

*a.* Compounds only in the molten or dissolved state exhibiting a rotatory power, which therefore must be an immediate manifestation of the dissymmetry of the molecules.

*b.* Compounds whose crystals show a rotatory power and hemihedrism, but whose solutions are optically inactive.

*c.* Substances which exhibit a rotatory power, both in solution and in the crystalline state. Among classes *b* and *c* a further distinction can be made between such crystals, the rotatory power of which is caused by pseudo-symmetrical intergrowth (Chapter VII), and where it is a characteristic property of their structure. The rotatory power of the last mentioned group may be quite different, and in opposite directions in the crystals and in the liquid state, as far as the rotation of the crystalline substance is an inherent property, and not caused by pseudo-symmetrical intercalation.

Thus, according to Wyruboff<sup>3)</sup>, while for instance the rubidium-salt of dextrogyratory tartaric acid deviates the plane of vibration of the polarised light to the *right if dissolved in water*, the crystals of the substance are nevertheless *laevogyrate*. It is difficult to give a rational explanation of such facts, as the hypothesis of Liebisch<sup>4)</sup>, who attributes the phenomenon to the circumstance that in aqueous solution the salt is evidently

1) F. M. Jaeger, *Proceed. Kon. Akad. v. Wet. Amsterdam*, Vol. 17 and 18, (1915), *loco cit*; *Chem. Weekblad* 14. 726, 727. (1917).

2) W. J. Pope, *Zeits. f. Kryst. u. Miner.* 27. 406. (1896).

3) G. Wyruboff, *Journ. de Phys.* (3). 3. 451. (1894).

4) Th. Liebisch, *Grundzüge der physik. Krystallographie*, (1896), p. 428.



dissociated, while in the crystalline state it is not, — can hardly be maintained considering Rimbach's measurements<sup>1)</sup> on the subject. This author found that *rubidium-d-tartrate*, if *not* dissociated, shows in solution a rotatory power of:  $\alpha = + 25^{\circ},63$ ; and if totally dissociated, of  $\alpha = + 19^{\circ},51$ . The crystals, however, are strongly *laevo*-gyratory:  $\alpha = - 10^{\circ},7$ , so that the influence of the spiral molecular arrangement in the crystals far outweighs that of the molecules themselves.

With respect to group *a*, the absence of rotatory power in the crystals of these substances may be considered to be a quite accidental case, and of only secondary importance. As a rule we may suppose that substances of this kind will ordinarily behave like those of group *c*.

We have now therefore only to draw attention to the compounds of group *b*. Their number is not very great, and of many of them it could be shown to be at least probable, that the rotatory power of their crystals is in numerous cases really caused by pseudo-symmetrical intergrowth of lamellae<sup>2)</sup>, in the same way as rotatory power is exhibited by the well-known mica-piles of Reusch. In the previous chapter (p. 181, etc.) we have dealt with these facts more in detail.

In every case, — as soon as crystals of *sodium-chlorate*, *sodium-bromate*, *sodium-dihydrophosphate*, Schlippe's salt, *sodium-uranyl-acetate*<sup>3)</sup>, etc. are dissolved in water, the optical activity entirely disappears. From this the conclusion has often been drawn that the optical activity is merely due to the spiral arrangement of the crystal-molecules, this involving a *laevo*-, respectively a *dextro*-gyratory helicoidal assemblage which breaks down as soon as the crystals are dissolved<sup>4)</sup>.

1) E. Rimbach, Zeits. f. phys. Chemie 16. 671. (1895).

2) G. Wyruboff, Ann. de Chim. et Phys. (4) 8. 412. (1886). E. Mallard, Bull. Soc. Miner. 7. (1884); 8. (1885); cf. also Chapter I'II.

3) For *sodium-uranyl-acetate*, however, the pseudo-symmetrical character seems also to be proved beyond any doubt.

4) It was discussed, however, by the author (Proceed. Kon. Acad. Amsterdam. Vol. 19. (1917); Chem. Weekblad 14. 723. (1917), that in systems of true antipodes sometimes phenomena may be observed which are completely analogous to those found in the case of *sodium-chlorate*; etc. The optically active forms of *potassium-rhodium-tri-oxalate* show abnormal rotation-dispersion, their specific rotation passing through zero for a wave-length of 5970 Å. U. For light of this special wave-length the ternary system of solvent and both antipodes behaves in

However Barker and Marsh<sup>1)</sup> have recently drawn attention to the fact that among these substances there are a number, which should have binary helicoidal axes, especially those belonging to the rhombic and monoclinic system. Such assemblages should only exhibit true enantiomorphism if the constituting units of the structure have themselves a non-superposable symmetry<sup>2)</sup>. According to these authors, this will apply to such cases as *sodium-chlorate* and *-bromate*, because their heteropolar ternary axes are always combined in pairs. They conclude from their reasonings that molecules such as  $\text{NaClO}_3$ ,  $\text{Mg SO}_4 + 7 \text{H}_2\text{O}$ , etc., must themselves have an enantiomorphous configuration.

To gain such a conception of the stereometrical configuration of inorganic salts such as the above mentioned, the authors take into account Werner's co-ordination-schemes. As might be expected in advance however, they only succeed in finding such stereochemical formulae in a few cases; thus in the case of *magnesium-sulphate* ( $+ 7 \text{H}_2\text{O}$ ), and of *sodium-chlorate*, while in far the most cases too little is known about the true constitution of the salts considered, to make such an attempt successful. Even in the case of the two salts mentioned, their suppositions seem rather hypothetical: thus for *magnesium-sulphate*  $+ 7 \text{H}_2\text{O}$ , one of the seven molecules must be considered as „constitution"-water, and the oxygen-atom is thought always to take the place of two co-ordination-loci, being in their opinion a substitute of a dyad character. When the atom is thought to be in the centre of eight co-ordination-places, divided in space as the corners of a cube, they demonstrate that of the three possible arrangements for the atom-complex:  $(\text{SO}_4, \text{H}_2\text{O})''$ , *two* will have the symmetry  $C_2^V$  and *S*, (*I* and *II*: *fig. 169*) but only *one* that of the axial group  $D_3$ ; *III* in *fig. 169*.

In their opinion, to  $(\text{Mg SO}_4, \text{H}_2\text{O}) + 6 \text{H}_2\text{O}$  could therefore only be attributed the configuration *III*; and in an analogous way they deduce for the  $\text{ClO}_3^-$ , resp.  $\text{BrO}_3^-$ -ion a configuration quite analogous to that of Werner's *tri-ethylenediamine*-salts ( $D_3$ ), in

apparently the same way as the binary system built up from the components: solvent  $+ \text{sodium-chlorate}$ . This is valid, however, only for that one, singular point of the system, and only for a definite temperature and pressure.

1) Th. V. Barker and J. E. Marsh, Journ. of the Chem. Soc. London **103**. 837. (1913).

2) Cf.: St. Kreutz, Elemente der Krystallstruktur, I. p. 83,90. (1915).

which ions the central halogen-atom then should be heptavalent.

As long as no exacter data about the configuration of inorganic salts are at our disposal, such applications of Werner's theory are not much promising<sup>1)</sup>.

However the idea that the optical inactivity of the solution should be caused by a very rapid auto-racemisation during the process of solution of the salt, is used by them in a very suggestive way to explain the dimorphism of  $NaClO_3$ , discovered by Mallard<sup>2)</sup>. This author observed a second unstable modification of the cubic salt, isomorphous with the rhombohedral sodium-nitrate. If now  $NaNO_3$  be supposed to be a racemic compound, its rhombohedral crystals being pseudo-racemic intergrowths of *d*-, and *l*-forms of cubic symmetry, the ditrigonal second form of sodium-chlorate found by Mallard, would then

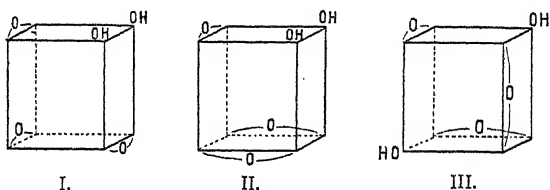


Fig. 169.

be the racemic form of this salt, and its transition-temperature might be thought entirely comparable to the temperature at which the racemic compound is resolved by spontaneous crystallisation, just as this occurred in the case of sodium-ammonium-racemate below its transition-temperature.

Although the idea is quite original, it can hardly be denied that there is much artificiality in the application of the co-ordination-theory in such cases. Notwithstanding this, one fact may perhaps be brought to the fore, which might support the above mentioned view in some respects: the addition-compound of ethyl-piperidine and propyl-iodide (or of propyl-piperidine and ethyl-iodide), i. e. the ethyl-propyl-piperidonium-iodide (mpt: 276° C) which was studied by de Brereton Evans<sup>3)</sup>, presents apparently

<sup>1)</sup> Cf. The critical remarks of A. W. Stewart in his *Recent Advances in Physical and Inorganic Chemistry*, London, (1912). p. 165, 173, etc.

<sup>2)</sup> E. Mallard, *Bull. de la Soc. Miner.* **7**. 352. (1884).

<sup>3)</sup> C. de Brereton Evans, *Journ. Chem. Soc. London* **71**. 522. (1897).

a case quite analogous to that of *sodium-chlorate* in so far, as it can easily be obtained in enantiomorphous crystals of monoclinic symmetry, both of which however give absolutely *inactive* solutions. The crystal-forms are reproduced in *fig. 170 a* and *b*; they have the symmetry of the group  $C_2$ .

Just as in the case of *sodium-chlorate*, it was here also noticed that when *a few large* crystals separated from the solution, these were nearly always *of the same kind*, whereas a large crop of *small* crystals generally consisted of both forms in about equal numbers.

Now in the case considered there is indeed every probability that to the enantiomorphism of the crystal-forms, corresponds a real enantiomorphism of the atomic arrangement in the constituent

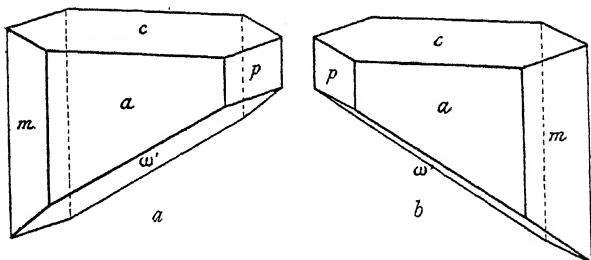


Fig. 170.

*Ethyl-propyl-piperidonium-iodide.*

molecules: for we have here evidently to deal with a *derivative of a pentavalent, asymmetric nitrogen-atom* which, as we have seen, *can* in many cases exhibit a true molecular dissymmetry (p. 233). There is every probability here that the explanation suggested above is valid in this case, and the great analogy of this behaviour with that of the *sodium-chlorate*-crystals could easily persuade us to adopt in the last case also a similar interpretation of the phenomenon, as might be given for the *piperidonium*-derivative.

In any case it seems worth while to keep these facts in mind, and to gather more instances before rejecting completely the ideas discussed above.

§ 30. If we review once more what the considerations dealt with in this chapter have led to, we may say that the meaning of Pasteur's famous law has become appreciably clearer after

all the investigations of the last decenniums, than it must have appeared at the time when it was formulated by the great French discoverer. In our opinion we may perhaps state these results in the most concise way by summarising the typical features as follows:

1). An atomic arrangement in chemical molecules which has only axial symmetry, involves the property of a possible fission into enantiomorphously related isomerides endowed with optical rotatory power.

2). If a chemical compound possesses a single asymmetric plurivalent atom ( $v > 3$ ) in the sense of Van 't Hoff and Le Bel's theory, all conditions are present to make the compound resolvable into such enantiomorphously related isomerides endowed with optical rotatory power.

3). The possibility of a fission as indicated is however *not* necessarily restricted to the special case of the existence of an asymmetric plurivalent atom; it is, contrary to this view, merely dependent upon the presence of a stereometrical configuration which has *only axial symmetry*, and this may also occur if no asymmetric atoms whatever, in the sense of Van 't Hoff and Le Bel's theory, be present. Reversely: even if several of such asymmetric atoms be present in the molecule, it *may* occasionally be optically *inactive* and *non-resolvable* into enantiomorphous antipodes.

4). The magnitude of the optical rotation seems to be determined for a good deal more by the configuration in space, than by the chemical contrast between the substitutes; the nature of the plurivalent central atom however appears to be also of predominant significance therein.

5). The non-superposable hemihedrism of the two antipodes in the crystalline state, as postulated by Pasteur, is a phenomenon which in most cases runs parallel to the occurrence of optical rotatory power, but it is not always necessarily manifested with it. It is undeniable that there is often a parallelism between the two phenomena, but sometimes it may seem that there is no such parallelism. The degree of non-superposable hemihedrism seems to be chiefly dominated by the chemical contrasts between the different substitutes, and perhaps has only an indirect relation to the absolute magnitude of the optical rotatory power as exhibited by the molecule in the dissolved state.

6). The general agreement between experience and theoretical deduction as founded on the conceptions of Van 't Hoff and Le Bel's theory regarding the stereometrical configuration of the atoms in the molecules, proves that these stereometrical formulae are not merely rough schemes, but that they even give a fairly exact idea of the really existing geometrical relations in such molecules, especially with respect to their configuration in space.

In the following chapter some other problems intimately connected with Pasteur's law will be considered more in detail.

## CHAPTER IX.

### PASTEUR'S LAW (*continued*).

The Production of Racemic or Externally Compensated Substances from Inactive Materials. — Chemical Reactions in which Optically Active Substances play a Rôle. — The Rotatory Power of the Reaction-products in comparison with that of the original Substances. The Walden-Inversion: Facts, Problems, Explanations. — Reaction-velocity of Antipodes attacking Optically Active or Inactive Substances. — Artificial and Natural, or Symmetrical and Asymmetrical Synthesis. — Production of Optically Active Substances from Inactive Materials, influenced by other Optically Active Substances. — Partial and Total Asymmetrical Synthesis. — The Final Problem. — Experiments on Partial Asymmetrical Synthesis. — The Directional Influence of Asymmetry or Dissymmetry, already existing, upon the Resulting Dissymmetry of the Molecule. — Asymmetric Conditions during Synthesis. — Problems to be solved in Future. .

*"Les produits artificiels n'ont donc aucune dissymétrie moléculaire; et je ne saurais indiquer l'existence d'une séparation plus profonde entre les produits nés sous l'influence de la vie, et tous les autres.... Il y a là des mystères, qui préparent à l'avenir d'immenses travaux et appellent dès aujourd'hui les plus sérieuses méditations de la science".*

L. Pasteur, 1860.

§ 1. In the preceding chapter we have already had occasion to draw attention to the fact that special methods alone enable us to obtain optically active substances from racemic compounds or from externally compensated mixtures. Indeed, in all our chemical reactions, as seen in our laboratories, we can only pro-

duce optically inactive substances, if we start from the ordinary, optically inactive re-agents. The explanation of this is, that the mechanical stability of both enantiomorphous atomic configurations with respect to forces which have themselves a symmetry of the second order, is evidently the same, and therefore the chance that both enantiomorphous molecules be produced by such forces, is the same also. Thus in our ordinary chemical reactions between optically inactive molecules, equal quantities of both molecules will be produced in a certain lapse of time; or at least, the accidental deviations from equal quantities will be so slight that the final product will appear optically inactive, even if examined by our most exact experimental methods.

On the other hand, because, starting from optically inactive materials we can in our chemical laboratory processes only produce optically inactive substances which, — if resolvable at all, — can be separated into their antipodes by only a few and moreover delicate and tiresome manipulations, — we can from this assume, that in all probability the agencies which play a rôle in such chemical processes, have really such symmetry-properties of the second order, and that in consequence they determine chemical and physical conditions during the reaction, which do not differ from the mirror-images of these special circumstances.

Of course, conditions are different when optically active molecules take part in the reaction. Here we can distinguish three cases:

*a.* An optically active substance acts upon an optically inactive, non-resolvable compound, in such a way that there is merely a substitution of one of the atoms or radicals placed round the asymmetric carbon-atom of the active molecule by another atom or radical.

*b.* An optically active compound acts upon an optically inactive substance in such a way that a new asymmetric carbon-atom is produced in the active molecule besides the one already present.

*c.* An optically active compound acts upon another optically active substance, or upon an inactive, racemic or externally compensated substance.

We shall consider these three cases in the following paragraphs.

§ 2. If an optically active molecule acts upon an optically inactive, non-resolvable substance in such a way that one of the atoms or radicals placed round the asymmetric carbon-atom is substituted by another group or atom, then a product will generally



be obtained, which itself is also endowed with rotatory power. Whether this will be greater or smaller than that of the original substance, cannot be predicted, because general rules concerning the influence of the chemical nature of substitutes on the size of the specific or molecular rotation of the molecule in solution, have up till now not been established with great success.<sup>1)</sup> As already mentioned, a number of experimental investigations of this kind have been made by Guye, Walden, Patterson, Frankland, Rupe, and many others; but definite laws which might hold in all cases, have not yet been found.

If no racemisation occurs during the reaction, we can suppose that the new configuration in space will in general correspond to that of the original antipode; however this is certainly not always the case, as a change of place of the radicals round the asymmetric atom during the reaction must indeed be considered a strong possibility. Racemisation under such circumstances is not seldom observed, especially if a *phenyl*-group be directly linked to the asymmetric carbon-atom; --- so that the final reaction-product appears to be inactive. This sustains the view that a certain "mobility" of the substitutes round the asymmetric atom must be supposed, which under favorable circumstances may lead to a complete interchange of place between the four radicals round the asymmetric central-atom, and to a final re-arrangement in such a way as to reproduce the enantiomorphous configuration of the original molecule.

But even if *no* such change of configuration as is pictured here, take place during the process, we are by no means sure that the optical rotation of the obtained product will not have the opposite algebraic sign to that of the original molecule. Instances of this are well known: the salts of many optically active acids show a rotation opposite to that of the acid itself, and the same may be the case when organic optically active bases are transformed into their salts by addition of ordinary inorganic acids

Thus the *zinc*-salt of *dextrogyrate lactic acid*<sup>2)</sup> is *laevogyrotory*,

1) The theoretical development of the phenomenon of optical rotation is yet far from being accomplished; see about this: G. H. Livens, *Phil. Magaz.* (6). **25**. 817. (1913); **26**. 362, 535. (1913); **27**. 468, 994. (1914); **28**, 756 (1914); M. Born, *Dynamik der Krystallgitter*, (1915).

2) E. Fischer and A. Skita, *Zeits. f. physiol. Chemie* **33**. 190. (1901).

and the same is true for the sodium-salt of dextrogyratory  $\alpha$ -nitro-camphor; laevogyrate glycerinic acid gives a dextrogyrate calcium-salt<sup>1)</sup>. The chlorohydrate of dextrogyrate  $\alpha$ -amino succinic acid is laevogyratory<sup>2)</sup>; and the opposite rotations of the derivatives of aspartic acid are well-known, according to the event that the  $H$  of the  $COOH$ -group be replaced by metal-atoms, or that a salt be formed by addition of an acid to the amino-group<sup>3)</sup>. In these cases the circumstances during the chemical process are such as to make a re-arrangement of the original molecule highly improbable, because with a few precautions each change of temperature may be avoided. The problem of explaining the change of sign of the rotatory effect after substitution, cannot be solved at present, as we are still waiting for a sufficient dynamical explanation of the molecular rotatory power in its dependence on the dissymmetrical arrangement of the atoms in the molecule. Here lies a problem of the highest interest and urgency for mathematical physicists, and it is to be hoped that some advance will be made in this difficult matter within not too remote future.

§ 3. In this connection we have however to consider a phenomenon which is also of high importance for the problems with which we shall have to deal further-on in this chapter. I mean the remarkable *inversion* discovered by Walden<sup>4)</sup> in 1896, and which may best be elucidated by some examples.

If in laevogyratory malic acid, the hydroxyl-group be replaced by chlorine, a dextrogyratory chloro-succinic acid results. This in itself is not particularly remarkable, because in accordance with what has been said above, both substances *can* have analogous configurations in space, notwithstanding their opposite rotations. But if this chloro-succinic acid is transformed into malic acid again, the last appears to be this time the dextrogyratory antipode. In this process there must have occurred at least *one* inversion, as the dextro- and laevogyratory malic acids have certainly enantiomorphous configurations. It is however questionable whether the inversion took place during the change of the malic acid into

1) E. Fischer and W. A. Jacobs, Ber. d. d. Chem. Ges. **40**. 1068. (1907).

2) E. Fischer and K. Raske, Ber. d. d. Chem. Ges. **40**. 1053. (1907).

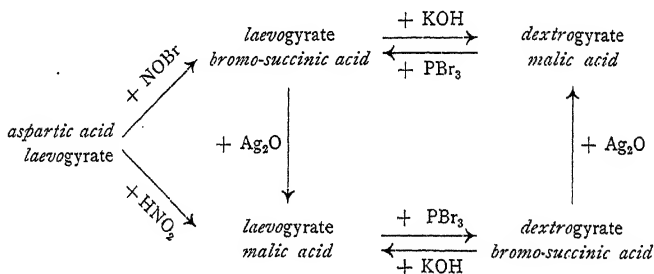
3) V. Meyer and P. Jacobson, Lehrb. d. Organ. Chemie, 2e Aufl. I, 2. 778, 779, (1913).

4) P. Walden, Ber. d. d. Chem. Ges. **29**. 133. (1896); **30**. 2795, 3146. (1897); **32**. 1833, 1855. (1899); **40**. 2470. (1907); etc.

the *chloro-succinic acid*, or during the transformation of the last acid into the final dextrogyrate *malic acid*. Moreover, it is most remarkable that the inversion is evidently intimately connected with the particular nature of the substance by which the *chloro-succinic acid* is finally transformed into the *malic acid*; for if *silver-oxide* or *silver-carbonate* be used for this purpose, the final product is the *dextrogyratory malic acid*, while, when *potassium-hydroxide* or *ammonia* is used in the reaction, the original *laevogyratory acid* is reproduced.

Quite independently of the question, as to whether or not a re-arrangement of the groups round the asymmetric carbon-atom takes place in the transformation of *l-malic acid* into *d-chloro-succinic acid*, or in that of the latter into one of the enantiomorphous *malic acids*, an "inversion" must obviously have occurred during the process.

It is possible, as has been pointed out by several investigators<sup>1)</sup>, to pass through a complete *cycle* of such changes, if the corresponding reactions be only suitably chosen. As an example of this the following cycle may be mentioned:



If *laevogyratory aspartic acid* be treated with *nitrosyl-bromide*, it is changed into the *laevogyratory bromo-succinic acid*; this however will be changed by an aqueous solution of *ammonia* into the *dextrogyrate aspartic acid*. By the same succession of reactions the latter will now be transformed into the original *laevogyrate acid*, etc.

These highly remarkable "inversions" have been observed almost

<sup>1)</sup> P. Walden, *loco cit.*; Journ. de Chim. phys., **9**, 164, 176. (1911); A. Mac Kenzie and G. W. Clough, Journ. Chem. Soc. London, **93**, 811. (1908); **95**, 777. (1909); **97**, 1016, 2564. (1910); **101**, 390. (1912); P. F. Frankland, Journ. Chem. Soc. London, **103**, 713. (1913).

exclusively in cases in which the atoms and radicals:  $Cl$ ,  $Br$ ,  $OH$ , and  $NH_2$ , when linked directly to the asymmetric carbon-atom, are replaced by interchanges; however, as has already been said, the occurrence of a change of the optical rotation from positive to negative, or vice versa, is greatly dependent on the re-agents employed in the transformations.<sup>1)</sup>

Fischer<sup>2)</sup> has made an application of the inversion produced by the mutual substitution of *halogen*-atoms and the *amino*-group, for the purpose of obtaining both the antipodes of racemic *polypeptides*, as for instance in the case of *l-alanyl-glycine*.

A certain, although small number of regularities have been found. Thus the substitution of *hydroxyl*-groups in *hydroxy-acids* and their *ethers* by  $Cl$  or  $Br$ , is commonly connected with a change of the rotatory effect from positive to negative, and vice versa, if  $PCl_5$  and  $PBr_5$  be used in the reaction. An exception to this rule which in many cases appears to hold good, was found by Guye and Jordan<sup>3)</sup>, who showed that the *laevo*-gyratory *isobutyl-ether* of *normal- $\alpha$ -hydroxy-butyric acid*:  $CH_3.CH_2.CH(OH).COOC_4H_9$ , was transformed by  $PCl_5$  into a *laevogyratory* chlorinated, but by  $PBr_5$  into a *dextrogyrate* brominated derivative. However even in this case it is by no means certain that these two cases also correspond to a real difference in configuration; for it is quite possible that if both  $Cl$  and  $Br$  came into the same place in space as the  $HO$ -group before occupied, the respective substitution-products would yet have oppositely directed rotations.

Moreover, in replacing *halogen*-atoms by *hydroxyl*-groups, the remarkable difference between the action of  $Ag_2O$  and  $KOH$ , as already stated above, has been repeatedly observed. According to Biilman<sup>4)</sup> this difference of action is intimately connected with the fact that the reaction with *silver*-compounds goes on very rapidly, while that with *potassium-hydroxide* on the contrary very slowly. The rapid change would occur without a change of con-

1) Cf. O. Lutz, Ber. d. d. Chem. Ges. **41**. 841. (1908); Zeits. f. phys. Chemie, **70**. 256. (1909).

2) E. Fischer, Ber. d. d. Chem. Ges. **39**. 2895. (1906); **40**. 489. (1907); Cf. also: E. Fischer and K. Raske, Ber. d. d. Chem. Ges. **40**. 1051. (1907); E. Fischer and H. Scheibler, *ibid.* **41**. 889, 2891. (1908); **42**. 1219. (1909); E. Fischer, H. Scheibler and R. Groh, Ber. d. d. Chem. Ges. **43**. 2020. (1916); E. Fischer, Chem. Zeitg. (1910), p. 825.

3) Ph. A. Guye and Ch. Jordan, Bull. de la Soc. Chim. (3). **15**. 495. (1896).

4) E. Biilmann, Ann. der Chemie, **338**. 335. (1911).

figuration, the slow one with a re-arrangement of the atoms in space.

*Mercuric oxide* also seems to act upon halogenated acids in the same way as *silver-oxide*.

The change of an *amino-acid* into an *hydroxy-acid* by means of *nitrous acid*, is a very quick reaction; therefore no change of configuration would take place here, and Biilmann concludes that the *aspartic acid* and the *malic acid* in plants would have the same arrangement in space of the groups placed round the asymmetric carbon-atom.

§ 4. But here we touch the problem under consideration at its very crux: for how can we be sure whether the original asymmetrical configuration has been changed during the process or not? If the reactions without change of configuration be named *normal*, and those accompanied by such a change *abnormal* substitutions, we may ask: when must a chemical reaction be considered as a normal and when as an abnormal one?

The answer to this question has occupied a number of chemists, because it is evidently closely related to the particular views on the mechanism of substitution in such asymmetric molecules, and several explanations of the Walden-inversion have been suggested by various authors.<sup>1)</sup>

Some of them, especially Armstrong, Gadamer, and Fischer, make the supposition that during the reaction instable intermediate compounds must necessarily be formed, in order to preserve a continuous asymmetry of the molecule, while the substitution takes place; and Fischer points out, that precisely the substitutes  $NH_2$ ,  $OH$ ,  $Cl$ , etc., with which the Walden-inversion ordinarily occurs, are those which have a "residual affinity". This enables them to form such intermediate compounds, which are then later decomposed, and the place vacated by the old

<sup>1)</sup> H. E. Armstrong, Journ. Chem. Soc. London, 69. 838, 1399. (1896); E. Fischer, Berl. Ber. 40. 492. (1907); Ann. der Chemie 381. 312. (1911) 386. 374. (1911); 394. 352. (1911); J. Gadamer, Chem. Zeitg. 34. 1004. (1910); 36. 1327. (1912); J. A. Le Bel, Journal de Chim. phys. 9. 323. (1911); A. Werner, Ber. d. d. Chem. Ges. 44. 873. (1911). E. Biilmann, loco cit.; P. F. Frankland, loco cit. p. 738; cf. also: G. Senter, Journ. Chem. Soc. London, 107, 638. (1915); 109. 1091. (1916); S. Arrhenius, Theorien der Chemie, 2e Aufl. (1909), p. 83; E. Mohr, Chem. Zeitg. 36. 984. (1912); P. Pfeiffer, Lieb. Ann. 388. 123. (1911).

substitute is occupied by the new one, or by one of the three already present.

Werner makes a suggestion to account for the phenomenon by supposing that the other substitutes have a guiding influence which tries, by means of attraction, to bring the new substitute into the range of the three others; the mechanism, as proposed by this author, does not involve any reference to the fact that one group would take the place formerly held by another.

The most recent investigations of Debye<sup>1)</sup> on the molecular structure of the *graphite*-crystal, made by means of Röntgen-rays, throw some new light also on the problem under consideration. Debye was able to demonstrate that the carbon-atom not only acts with *four* equal valencies which are directed in space as supposed by Van 't Hoff, but that this atom can also act with *three* valencies of equal strength, while the fourth is considerably reduced in comparison with the others, acting in a direction perpendicular to the plane of the last, and with only a very slight intensity. If this be true, we might suppose that during the chemical process a passing detachment of the radical takes place, and that as soon as the new substitute arrives, the restitution of this fourth reduced valency into the original state of four equal valencies can occur towards the one or towards the other side of the plane of the three others, both these events finally leading to two enantiomorphous tetrahedron-configurations.

Such an intermediate detachment of the radicals round the asymmetric atom, but under simultaneous formation of ethylene-derivatives, was also previously proposed by Nef<sup>2)</sup> in his explanation of phenomena of re-arrangement in general. It still however remains unexplained why such a change of place does not always lead to complete racemisation, as both antipodes have the same mechanical stability.

However, all these suggestions can hardly be considered otherwise than made "pour besoin de la cause", and to be hypotheses which in general appear quite arbitrary, although perhaps they are useful in some special cases. Frankland, in his summary of the facts up till now observed with respect to the remarkable and highly important phenomenon of the Walden-inversion, is un-

1) P. Debye; cf. note on p. 152.

2) J. U. Nef, Journ. Amer. Chem. Soc. **30**, 647. (1908).

doubtedly quite right, when he states: "it appears that there does *not* exist at the present time any criterion by which the relation between the configuration of an optically active compound and that of its derivative, can be decisively ascertained." All assumptions as to the occurrence or non-occurrence of a change of configuration during such a substitution, appear to be merely arbitrary and hypothetical.

Such assumptions for instance are: that the change of rotatory power from positive to negative, and vice versa, if  $PCl_5$  or  $PBr_5$  act upon *hydroxy-acids* or their *ethers*, is really accompanied by an inversion of the configuration round the asymmetric carbon-atom; that eventually the same takes place when the halogen-acids:  $HCl$ ,  $HBr$ , etc., themselves act upon such *hydroxy-acids*<sup>1)</sup>; that the same occurs when  $SOCl_2$  acts upon such molecules<sup>2)</sup>; that  $NOBr$  and  $HNO_2$ , acting upon *amino-acids*, do *not* cause a change of configuration<sup>3)</sup>; that on the other hand the substitution of  $NH_2$  by a *halogen*-atom is commonly accompanied by a change of configuration; etc. etc.

The question is undoubtedly enormously complicated. In truth, *every* substitution of an atom or radical by some other, must always have a distortion of the molecule as a necessary consequence; and every thing evidently depends on the relative effect of this distortion in comparison with that necessary to cause a real interchange of place leading to a consequent inversion of the stereometrical arrangement round the asymmetric carbon-atom.

The very important recent researches of Senter<sup>4)</sup> demonstrate convincingly that the difficulty is much greater yet than has been hitherto realised, and that the phenomenon itself is also much more complicated than was thought at first. This author found that, if in optically active *ammonium-phenyl-chloro-acetate* the *chlorine*-atom is substituted by an *amino*-group, optically active products will result, whose rotation is positive or negative, according to the special nature of the *solvent* taken as reaction-medium. He stated, for instance, that if *water* were used as a

1) A. Mc. Kenzie and H. B. P. Humpries, Journ. Chem. Soc. London **97**. 121. (1910); A. Mc. Kenzie and H. Wren, *ibid.* **97**. 1355. (1910).

2) A. Mc. Kenzie and F. Barrow, Journ. Chem. Soc. London **99**. 1923. (1911). R. H. Pickard and J. Kenyon, Ber. d. d. Chem. Ges. **45**. 1592. (1912).

3) E. Biilmann, Ann. der Chemie **388**, loco cit. (1911).

4) G. Senter, Journ. Chem. Soc. London, **107**. 638. (1915); **109**. 1091. (1916).

solvent, the product had the *opposite* direction of rotation to that of the original substance; whereas if *aceto-nitrile* were the solvent, the resulting *amino*-derivative showed a rotation of the same kind as before.

Later a dozen optically active solvents were investigated in this way, and the fact referred to above was plainly confirmed. Senter concludes that it is becoming more and more evident that a satisfactory explanation of the Walden-inversion is *not* likely to be reached at present, and that it must be considered premature to enter now upon a full discussion of the significance of the results obtained with respect to this highly interesting phenomenon which, beyond all doubt, also plays an important rôle in the chemical synthesis of the living organisms.

§ 5. Now we have to consider the two remaining cases: when an optically active molecule acts upon an inactive one so as to produce a new asymmetric carbon-atom in the already active molecule, and the other case, when an optically active molecule acts upon another optically active substance, or upon a substance which is either externally compensated or racemic.

Indeed, among these reactions we can safely include those, where an optically active substance also acts upon a racemic or an externally compensated substance. For as racemic compounds in solutions are at any rate dissociated to a large extent, or even totally, into their optical antipodes, and as inactive mixtures will of course only act therefore as if their right and lefthanded components were completely free, — the action of such inactive, resolvable substances upon optically active ones thus belongs here, and not among the cases dealt with in the preceding paragraphs.

In the first place we may remark that in general the affinity-constants of two antipodes  $A$  and  $A'$  with respect to another substance  $B$ , appear to be the same in all cases, even if  $B$  itself is an optically active compound. In the last case, however, there will be a certain *difference of reaction-velocities*, because the products formed are no longer mirror-images of each other. The *speed* with which  $AB$  is formed, need not be the same as when  $AB'$  is produced.<sup>1)</sup>

Therefore, if an optically active compound  $B$  acts upon a racemic or externally compensated substance  $AA'$  (or  $A + A'$ ),

1) Of course, the fact that the affinities are the *same* between  $A$  and  $B$ , and



and if the reaction, *before complete*, be stopped at a well-chosen moment, it will turn out that *unequal* quantities of  $AB$  and  $A'B$  will be produced during that lapse of time, and thus, if the mixture  $AB + A'B$  be isolated and  $B$  removed from it, the substance obtained  $AA'$  will be *no* longer optically inactive, but will show a positive or negative rotation, because there is now some excess of one of the antipodes  $A$  or  $A'$ . Of course, if the original compound  $AA'$  which has not yet combined with  $B$ , be examined now, it will also show an optical activity which is opposite to that found with the portion of  $AA'$  attacked, because there is now an excess of the other antipode  $A'$  or  $A$  in the mixture.

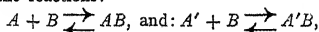
It has been stated in a few cases<sup>1)</sup> that the chemical affinity of both enantiomorphous molecules of the same compound, is the same, even towards an optically active compound.

Thus Fischer<sup>2)</sup> observed that there is *no* difference in the inversion-velocity of *cane-sugar* by *dextro-* or *laevogyrotory camphoric acid*. As the inversion-velocity is directly proportional to the concentration of the  $H$ -ions, this result cannot astonish us. The same appeared to be the case if *saccharose* were hydrolysed by *d-*, and *l-* *camphor-β-sulphonic acids*.<sup>3)</sup>

The two antipodes of an active acid will also divide an optically active base equally between them: in the end there will be 50% of the one salt and 50% of the other, if only the quantity of the added base be sufficient to neutralize the acid, and the reaction have time to reach its final equilibrium.

§ 6. A question of importance is: will there be a difference in the reaction-velocity of two antipodes when the reaction takes

between  $A'$  and  $B$ , need not exclude the possibility of *unequal reaction-velocities* in both cases. In the reactions:



the velocities are characterised by the velocity-constants  $k_1$  and  $k_1'$ , and  $k_2$  and  $k_2'$ . The affinities however are expressed by a relation of the form:  $RT \ln K$ , in which the equilibrium-constant  $K$  is the same for both reactions and equal to  $\frac{k_1}{k_1'}$  or to  $\frac{k_2}{k_2'}$ .

Now  $(k_1 - k_1')$  and  $(k_2 - k_2')$  can be very well *different* from each other, while the *quotients* are in both cases the *same*.

1) W. Marckwald and A. Chwolles, Ber. d. d. Chem. Ges. **31**. 783. (1898).

2) E. Fischer, Ber. d. d. Chem. Ges. **32**. 3617. (1899). Cf. also: W. Marckwald and A. Mc. Kenzie, *ibid.* **33**. 208. (1900).

3) R. Caldwell, Proceed. Roy. Soc. London, **74**. 184. (1904).

place in an optically active solvent? For if there be an active compound in any solvent, we always have to deal with such an active medium. Such an effect might be expected e. g., if both antipodes had a *different solubility* in the active solvent, or a *different diffusion-velocity*. As to the solubility, we have indeed some experimental data which seem to indicate that the influence of such a medium, if present at all, can only be very slight.

Tolloczo<sup>1)</sup> investigated the question whether *racemic acid* and *racemic mandelic acid*, if partitioning between an inactive and an optically active solvent, would show a partial separation into their antipodes. If *water* and *laevogyrotory amyl-alcohol* were used as solvents, no effect could be detected in the case of *racemic acid*, nor in that of the *mandelic acid*.

He concludes that the process of solution is in this case not accompanied by the formation of stronger or weaker compounds between solute and solvents.

Goldschmidt and Cooper<sup>2)</sup> determined the solubility of the optical antipodes of *carvoxime* in *dextrogyrate limonene* as a solvent, and could not find any certain differences. The partial separation of an externally compensated mixture of the *ammonium-sodium-tartrates* in solutions of *dextrose*, as described by Kipping and Pope<sup>3)</sup>, seems however a fact in contradiction with this, so that a new investigation of the solubilities under these circumstances appears necessary. On diffusion-velocities of active substances in optically active solvents no investigations have hitherto been made.

The experiments on the solubilities of such antipodes in active solvents just referred to, may give some insight into the causes of the negative results obtained hitherto in all attempts to find a difference in reaction-velocity for both antipodes, if optically active liquids be used as solvents.

The influence of the solvent on the reaction-velocity is still a very dark problem. It may be a pure "catalytic" one<sup>4)</sup>, in the sense in which this expression is commonly used when there is no further explanation possible for the questions at hand.

1) St. Tolloczo, Zeits. f. phys. Chemie **20**. 412. (1896).

2) H. Goldschmidt and H. C. Cooper, Zeits. f. phys. Chemie. **26**. 714. (1898); H. C. Cooper, Amer. Chem. Journ. **23**. 255. (1900).

3) F. S. Kipping and W. J. Pope, Proceed. Chem. Soc. London, (1897). p. 113.

4) J. H. Van 't Hoff, Vorlesungen ü. theor. u. phys. Chemie, I. (1898), p. 210, 216, 218.

If so, the final equilibrium will not be influenced by the presence of such a solvent, and there seems to be only a slight chance that any positive result may be expected from the experiments indicated above.

Secondly, the solvent may really take an active part in the reaction, for instance by means of the intermediate formation of instable compounds with the molecules of the re-acting substances. In such cases also an influence upon the final state of equilibrium will be present, or at least, may be present. If  $B$  represent the solvent, such a case may occur when there is an appreciable difference in solubility between the thus formed compounds  $AB_n$  and  $A'B_n$  in the optically active medium. But as we have seen in the preceding pages, this difference, if present at all, seems in general not to be very great, and even in this more favorable second case, therefore, no great expectations of positive results in experiments of the above mentioned kind should be had.

Experiments to demonstrate the existence of such differences in reaction-velocity, if the processes go on in a dissymmetrical medium, have already been made from time to time.

Thus Boyd<sup>1)</sup> tried to reduce *benzoyl-formic acid* by means of *hydrogen* in aqueous solutions of *dextrogyratory tartaric*, or *laevogyratory mandelic acid*; the *mandelic acid* produced in this reduction was completely inactive, or its activity corresponded to that of the active acid used in excess.

Kipping<sup>2)</sup> studied the reaction between  $KCN$  or  $HCN$ , and *benzaldehyde*, in an alcoholic solution of optically active *camphor*, or the reduction of *pyruvic acid* in an aqueous solution of *d-glycose*; the results were equally negative. E. and O. Wedekind<sup>3)</sup> investigated the addition of *allyl-iodide* to *methyl-benzyl-aniline* in optically active *limonene* as a solvent, but they could only obtain optically inactive products, and the same was true, when they used as solvents *l-menthol* or *l-chloro-methyl-menthyl-ether*.

From these experiments it may be concluded that it is highly improbable that a positive difference in reaction-velocity would be observed in the case of both antipodes, when optically active

1) D. R. Boyd, Inaug. Dissert. Heidelberg, (1896).

2) F. S. Kipping, Proceed. Chem. Soc. 16. 226. (1900).

3) E. and O. Wedekind, Ber. d. d. Chem. Ges. 41. 456. (1908).

liquids are used as solvents, namely, so long as they do not themselves take part in the reactions. This may also be concluded from the experiments of Bredig and his collaborators: thus Bredig and Balcom<sup>1)</sup> stated, that *d*- and *l*-campho-carboxylic acids are split into *camphor* and *carbon-dioxide* equally quickly when dissolved in *d*-, or in *l*-limonene. But, as we shall see later, as soon as optically active bases (like *quinine*, *quinidine*, *nicotine*, etc.) are used in this case as solvents, which undoubtedly take part in the reaction, combining with the acids to form intermediate compounds, — the differences in reaction-velocity of both antipodes can clearly be demonstrated, as we shall see in the following paragraphs.

§ 7. Thus, if the components *A* and *A'* really combine with the active molecule *B*, a difference in reaction-speed will most probably be found, notwithstanding the equal affinity of both antipodes towards *B*, because there is some guiding influence of the pre-existing dissymmetry of *B* in the formation of the compounds *AB* and *A'B*.

It is on this principle that the new method of fission of racemoids, proposed in 1899 by Marckwald and Mc. Kenzie<sup>2)</sup>, was founded; and it is this difference in the velocity of formation, as a consequence of the directing power of a pre-existing dissymmetry, which doubtless gives the explanation of the apparent difference between *artificial* and *natural* synthesis, with which we shall now have to deal somewhat more in detail.

Indeed, in the preceding chapter we have had occasion to see how in the laboratory optically active substances can only be obtained from inactive materials, if one of the special methods of fission proposed by Pasteur is suitably applied. If in artificial synthesis we start with optically inactive materials, we only can get optically inactive compounds, — even when a new asymmetric carbon-atom is produced in the molecule under investigation.

Our synthetic products are always racemic substances or externally compensated mixtures; and the explanation of this has always been given by drawing attention to the fact that in reactions, in which only symmetrical causes play a rôle, enantiomorphously related molecules must have the same mechanical

1) G. Bredig and R. W. Balcom, Zeits. f. phys. Chemie **41**, 740. (1908).

2) W. Marckwald and A. Mc. Kenzie, Ber. d. d. Chem. Ges. **32**, 2130. (1899).

stability. This very assumption has been the principle which led to the discovery of our usual fission-methods by P a s t e u r.

It must however be clear on closer examination that, properly speaking, in these methods of fission we always make use, in the last instance, of the *phenomena of life*, as manifested in the chemical synthesis which occurs in the cells of animals and plants. If we leave the method of fission by spontaneous crystallisation aside for the moment, we can only use for our purpose: either the combination of racemoids with the optically active acids or bases which are isolated from plants or animals; or we make use of the apparently selective action of ferments and enzymes which also are only produced by living cells

The living plant or animal, in striking contrast to what we observe in our laboratory-experiments, seems to produce directly from inactive materials such as *carbon-dioxide*, *water*, *ammonia*, etc., the optically active substances which are met with in its organism, unaccompanied by their optical antipodes.

The majority of *proteids* are laevogyrotory, the *bile-acids* dextrogyrotory. Plants always produce the same optically active *coniine*, *nicotine*, *strychnine*, etc., and the quantitative experiments of Brown and Morris<sup>1)</sup> on the formation of the *carbohydrates* in plants seem to prove beyond doubt, that exclusively *d-glycose* and *d-fructose* are produced in vegetable cells, not their laevogyrate antipodes. The direct production of optically active substances seems to be the very prerogative of life therefore; and the cases are extremely rare, where racemic compounds are met with in the living tissues.

An exception of this is found in the case of *pinene*, extracted from the leaves of *Myristica fragrans* Htn, which, according to Van Romburgh<sup>2)</sup>, sometimes is *laevogyrotory*, sometimes *dextrogyrate*, — it being impossible to tell under what particular circumstances the one or the other of the antipodes is produced.

Neuberg<sup>3)</sup> found, that an *inactive pentose* was excreted by the human organism in some cases of so-called "pentosuria", — which, however, according to af Klercker, is a mixture of the

1) H. T. Brown and G. H. Morris, Journ. Chem. Soc. London, **63**, 604. (1893).

2) Private communication to the author by prof. P. van Romburgh.

3) C. Neuberg, His-Engelmann's Archiv, Physiol. Abth., (1902), p. 544; idem, Der Harn I. p. 370. (1911); Ber. d. d. Chem. Ges. **33**, 2243. (1900).

racemic compound with an excess of the *laevogyrate* component <sup>1)</sup>, while Elliot and Raper <sup>2)</sup> find it more closely related to a dextrogyrate *ribose*, than to a racemic *arabinose*, as Neuberg thinks it to be.

From this the impression is left that, notwithstanding the enormous development of organic synthesis since the days of Liebig and Wöhler, there still remains a deep gulf between natural and artificial synthesis. The plant, that mysterious and highly complicated laboratory, produces from the simple inactive constituents of the atmosphere and the soil, within a very limited range of low temperatures moreover, the necessary *carbohydrates*, *proteids*, etc., in their optically active forms.

"I know of no more profound difference than this between common substances and those produced under the influence of life", — Pasteur wrote again in 1860; and apparently he was quite justified.

Natural, in contrast to artificial synthesis, thus appears to be a strictly "one-sided" or "asymmetrical" synthesis, and moreover of a very *exclusive* nature too. All attempts to isolate *laevogyrate* *glucose* or *fructose* from plants, have hitherto failed <sup>3)</sup>, neither has there been any success with any of the other optically active products of vegetable or animal bodies. A living world, the mirror-image of the one known to us, seems to be a grotesque phantasy. What would be the consequences of an eventual sudden inversion of all synthesis in plants and animals, as we now know it? "What world would be presented to our eyes", — asks Pasteur, — "if the *cellulose* turned from a *right-handed* to a *left-handed*, the *blood-albumine* from a *laevogyrate* to a *dextrogyrate* substance?" Indeed, if such circumstances could be realised in the living tissues, investigations of unlimited range would be open to the future, and at present such questions, are worthy of the most careful attention of scientists. However, so far, we can only state the rigorous and remarkable constancy of character of the chemical world in plants and animals. The living world is "specific" in its dissymmetry, and its dissymmetrical specificity is

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1) K. O. af Klercker, Deutsches Archiv. f. Klin. Medizin, **81**. 284. (1912). Cf. also: R. Luzzatto, Archiv. f. exper. Pathol. und Pharmacol., Suppl. Bnd. (1908), p. 366.

2) J. H. Elliot and H. S. Raper, Journ. Biol. Chem. **11**. 211. (1912).

3) E. Fischer, Ber. d. d. Chem. Ges. **27**. 3230. (1894).

of the highest degree. For P a s t e u r, chemical compounds of one-sided dissymmetry could not arise, save under the influence of life; and in this difference between artificial and natural synthesis, the great master of natural science saw the most characteristic property which, in his opinion, perhaps establishes to-day the only sharp line of demarcation between the chemistry of inanimate and that of living nature.

However, this contrast, so striking in aspect, is only an apparent one. P a s t e u r's vitalistic views were for a comparatively short time again adhered to by a number of partisans, especially by biological investigators. To these this asymmetrical synthesis in living organisms appeared to be quite inconceivable, and they were obliged to suppose a particular dissymmetry of the forces and influences acting in the living cells, different from those which take part in our synthetic laboratory-processes. Vital agency would include possibilities which are not only phenomenally, but also essentially, different from those offered to us by the so-called "dead" forces.

It is hardly necessary to repeat here the interesting controversy between vitalists, chemists, philosophers, etc., which was started in 1898 and 1899 by Japp's address to the British Association on "Stereochemistry and Vitalism"<sup>1)</sup>, to show the interest widely provoked by these problems.

And although, as we shall see, the last and most fundamental problem here is as yet only solved *indirectly*, and the striking evidence of these possibilities must again be brought by direct experiment, it can no longer be denied that during the last twenty years the apparent barrier between artificial and natural synthesis has mostly been removed, and that it has become more and more evident that in this respect also a fundamental contrast does *not* exist.

§ 8. E. Fischer<sup>2)</sup> was the first who pointed out the fact that so strong a contrast between natural and artificial synthesis,

<sup>1)</sup> F. R. Japp, Chem. News 77. 139. 149. (1898); G. F. Fitz Gerald, Nature, 58. 545, 59. 76. (1898 and 1899); C. O. Bartrum, *ibid.* 58. 455, H. Spencer, *ibid.* 58. 592; 59. 29; K. Pearson, *ibid.* 58. 495; 59. 30, 125; G. Errera, *ibid.* 58. 616; W. M. Strong, *ibid.* 59. 53; F. S. Kipping and W. J. Pope, *ibid.* 59. 53; P. F. Frankland, *ibid.* 59. 30; F. J. Allen, *ibid.* 58. 520; F. R. Japp, *ibid.* 58. 616; 59. 29, 54. 101; C. Ulpiani and S. Condelli, Gazz. Chim. Ital. 30. I. 344. (1900).

<sup>2)</sup> E. Fischer, Ber. d. d. Chem. Ges. 27. 3230. (1894).

as believed by Pasteur, may not be supposed. He drew attention to the fact that artificial synthesis also is evidently one-sided, as soon as there are *several* asymmetric carbon-atoms in the attacked molecule. Indeed, if this were *not* true, the progressing condensation of *glycerose*, *formaldehyde*, or *acroleine-bromide*, would necessarily lead to *all* sixteen possible isomeric *aldoses* and *all* the eight *ketoses*. Instead of this, besides  $\alpha$ -*acrose*, only a single racemic *hexose* is obtained; and this, clearly proves that there is a certain *preferential* direction in the synthesis of these sugars under these conditions. The same must be the case in the important *cyanhydrine*-reaction; when a certain dissymmetry of the reacting molecule pre-exists, the addition of *HCN* no longer occurs in a symmetrical way. Thus in using *mannose*, the one antipode of *mannoheptonic acid* <sup>1)</sup> was obtained to an amount of 87%, whereas of the other no appreciable quantity was found.

With this evidence Fischer undoubtedly for the first time brought clearly to the fore the essential features of "asymmetric" synthesis in general. Natural synthesis in the living organism takes place in a one-sided way, *because it occurs under collaboration of optically active molecules*; the dissymmetrical arrangement of such molecules taking part in the chemical processes has a *guiding* influence, and thus a single optically active compound of a whole set of isomerides is formed in greater quantity than the others.

However, it would perhaps be preferable to draw attention more particularly to the *differences in speed* in the process of synthesis of the isomeric substances. For the possibility of life-processes is at bottom, — from a chemical point of view — a question of the mutual regulation of reaction-velocities: the organism cannot stop its physiological functions for a single moment. It produces and consumes continually, and these processes of synthesis and metabolism, of waste and production, must all go on with definite, well regulated mutual velocities, if the life-process is to be carried on at all. A state of completed "reaction-equilibrium" is *never* reached therefore: only a kind of apparent "dynamical constancy". Now it is most probable that other isomerides than those found in the vegetable cells, are formed simultaneously in the synthetic process, but with an incomparably smaller speed. It is possible that there are exceedingly small

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<sup>1)</sup> E. Fischer, Ber. d. d. Chem. Ges. 22. 370. (1889).



amounts of these isomerides formed in a certain lapse of time, or perhaps that they are slowly eliminated, while the other antipode is taking part successfully in the common physiological reaction-scheme of the organism. It is more a question of strongly deviating velocities, than of extreme differences of quantity. If complete equilibrium could ever be reached during these processes, perhaps in the end we should really meet with equal or comparable quantities of both isomerides. But as has already been said, such a state will never be reached, as the life-process is continuously going on.

Now Fischer supposes that the asymmetric substances in the *chlorophyll*-grains primarily combine with the *carbon-dioxide*, or with the *formaldehyde* produced from it; and the following condensation to form sugars will then occur in an asymmetrical and preferential way, because of the directing influence of the pre-existing molecular dissymmetry. The products formed are used up in the life-process of the plant as fast as they are made. The "asymmetric forces" of Pasteur need *not* be looked for *outside* the organism, for they are determined by the chemical system *in* its cells, and these dissymmetrical influences *in* the living organism itself far outweigh the dissymmetrical agency of externally applied forces. All attempts to counterbalance or even to surpass these chemical directing influences, have hitherto signally failed. Pasteur himself<sup>1)</sup> refers to these somewhat phantastic and unsuccessful experiments, when he tried in 1854 to influence the particular dissymmetry of vegetable synthesis by means of a clock-driven heliostat and reflector which reversed artificially the diurnal motion of the sun in the sky.

They were unsuccessful of course: for what is this feeble influence compared with the enormous power of atomic attraction? He had, as has been said occasionally, still to deal with the one-sided agencies in all their irresistible strength, as they were determined by the dissymmetry of the chemical system in the living cells from the beginning of time. As has strikingly been remarked: starting with a definite optically active compound, there is something analogous to "heredity" in the further progression of dissymmetrical configurations in a series of successive reactions. Perhaps if the original optically active substance had been the antipode of that which was the beginning of all the existing one-sided

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1) L. Pasteur, *Revue Scientifique* (3). 7. 3. (1884).

chemical synthesis in plants and animals, we should now be living in a world which would be the very mirror-image of *this* world, — and of course not a happier one than it is.

But here the last and most fundamental problem forces itself insistently on us: what was the origin of that first optically active substance which determined and predestinated the direction of natural synthesis for all later times?

In contrast with the contentions of vitalism, and quite in the line of what was said with respect to our present conception of the analogy between natural and artificial synthesis, we can only guess that the formation of that *first* dissymmetrical molecule-species was certainly *not* connected with that of the first "living" particle. Indeed, the formation of such an optically active molecule, either alone and unaccompanied by its antipode, or together with its racemic compound, can within the scope of our present views only have occurred by *dissymmetrical influences outside all living organism*.

The dissymmetrical\* synthesis under such conditions is the only *true* "asymmetrical synthesis"; we will distinguish it from that previously mentioned, by the name "total" asymmetrical synthesis.

Until such a total asymmetrical synthesis has directly been performed with success, we cannot claim that we really understand natural synthesis absolutely, or in its full significance.

§ 9. Experiments on *partial* "asymmetric synthesis", as discussed above, have however been successfully made during the last fifteen years. One of the first attempts of this kind was made in 1904 by Simon<sup>1)</sup>, who prepared the ether from inactive *lactic acid* and *laevogyrate amyl-alcohol*; saponification by means of *KOH* of the ether formed, gave however only an *inactive* acid. Simon concludes that evidently no partial separation of the racemic compound has taken place. If he had not completed the reaction, but stopped it, *before* equilibrium was reached, or if he had used a quantity of alcohol insufficient for total etherification, the result might perhaps have been better.

Frankland and Price<sup>2)</sup> made analogous experiments in 1897 with inactive *glycerinic acid* and *laevogyrate amyl-alcohol*, but they

1) L. Simon, Bull. de la Soc. Chim. Paris (3). 11. 760. (1894).

2) P. F. Frankland and A. S. Price, Proceed. Chem. Soc. 133. 9. (1897); Journ. Chem. Soc. 71. 353. (1897).

also obtained a negative result. The laevogyrate *amyl-alcohol* was then combined with inactive *dibenzoyl-glycerinic acid*; although the ether could be obtained in beautiful crystals, no fission of the acid was found after saponification.

The first positive results were obtained in 1899 by Marckwald and Mac Kenzie<sup>1)</sup>, who heated *racemic mandelic acid* with *l-menthol* at 155° C. for one hour; the remaining, not attacked acid appeared to be *laevogyrate*, while a *dextrogyrate* acid was obtained from the ether-mixture after incomplete saponification. This experiment clearly shows that the velocity of etherification of *laevogyrate mandelic acid* with *l-menthol* is *smaller* than that of the etherification of the *dextrogyrate* acid, and that in accordance with this fact, the ether of the more rapidly formed *dextrogyrate* acid is also more rapidly decomposed by saponification than the ether of the *laevogyrate* acid. This of course agrees with the character of the saponification-process, as that of an "equilibrium"-reaction: the ether which is more rapidly formed, must also be saponified more quickly, should the equilibrium-constant remain unchanged.

Fischer<sup>2)</sup> drew attention to the fact that his famous experiments of the action of *emulsine* on the mixture of both the enantiomorphous  $\beta$ -*methyl-glycosides*, or those of the action of the yeast-ferments on both the corresponding  $\alpha$ -*methyl-glycosides*, demonstrate the same principle as was brought to the fore by Marckwald and Mac Kenzie. The remark is undoubtedly true (Chapter VIII); the so-called "specificity" of *enzyme-action* is indeed only based upon a great difference in the rate of attack of either antipode by the same *ferment* or *enzyme*, which are always themselves dissymmetrical substances.

Marckwald and Mac Kenzie<sup>3)</sup> determined the ratio of etherification- and saponification-velocities of the *laevo*-, and *dextrogyrate mandelic acids* with respect to *l-menthol*, at a value of 0,90. If the saponification be *completed*, the free acid obtained is *inactive*, which is a fresh proof that both antipodes have *the same affinity*

<sup>1)</sup> W. Marckwald and A. Mac Kenzie, Ber. d. d. Chem. Ges. **32**. 2130. (1899); Cf. also: F. S. Kipping and W. J. Pope, Proceed. Chem. Soc. (1898), p. 113.

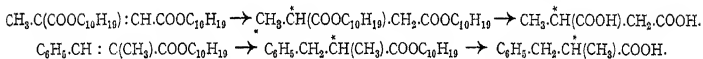
<sup>2)</sup> E. Fischer, Ber. d. d. Chem. Ges. **32**. 3617. (1899); W. Marckwald and A. Mac Kenzie, *ibid.* **33**. 208. (1900).

<sup>3)</sup> W. Marckwald and A. Mac Kenzie, Ber. d. d. Chem. Ges. **34**. 469. (1901).

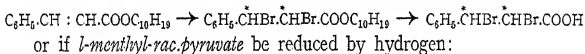
for the optically active *menthol*. *Laevogyrate octyl-alcohol* was etherified somewhat more rapidly by *dextrogyrate tartaric acid* than the corresponding *dextrogyratory octyl-alcohol*; however the last is etherified more rapidly by *laevogyrate tartaric acid*, as would be expected. The velocities of the saponification differ in this case appreciably more than the velocities of the etherification, — a difference much more pronounced here than in the case of the *menthol-mandelates* mentioned above.

In the year 1900 Cohen and Whiteley<sup>1)</sup> and later Kipping<sup>2)</sup> made some unsuccessful experiments of the same kind, and equally unfortunate were the attempts of Fischer and his collaborators<sup>3)</sup> in 1910, as well as those of Scholtz.<sup>4)</sup>

Cohen and Whiteley started with the *l*-menthyl-ethers of *mesaconic acid* and of *phenyl-crotonic acid*, and reduced them by addition of *hydrogen*-atoms at the double bond, thus producing a new asymmetric carbon atom (denoted by \*) in the molecule:



Analogous reactions take place if *bromine* be added to the double bond of the *l*-menthyl-, or *l*-amyl-ether of *cinnamic acid*:



or if *l*-menthyl-*rac*-pyruvate be reduced by hydrogen:



Something analogous was formerly proposed by Hartwall,<sup>5)</sup> who expected a one-sided synthesis by the reduction of the *citraconates* and *mesaconates* of optically active alcohols such as *menthol* or *borneol*; but he did not make experiments in this direction.

Kipping studied the addition of *hydrogen* to *quinine-pyruvate*, *quinine-levulinate*, *bornyl-pyruvate*, or to its *oxime*, and to *bornyl-*

<sup>1)</sup> J. B. Cohen and C. E. Whiteley, *Proceed. Chem. Soc.* **16**. 212. (1900); *Journ. Chem. Soc.* **79**. 1305. (1901).

<sup>2)</sup> F. S. Kipping, *Proceed. Chem. Soc.* **16**. 226. (1900).

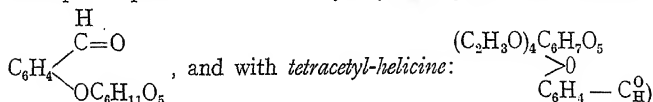
<sup>3)</sup> E. Fischer, *Ber. d. d. Chem. Ges.* **34**. 629. (1901); E. Fischer and M. Slimmer, *Ber. d. d. Chem. Ges.* **36**. 2575. (1903); *Sitzb. Ak. der Wiss. Berlin*, (1902), p. 597.

<sup>4)</sup> M. Scholtz, *Ber. d. d. Chem. Ges.* **34**. 3015. (1901).

<sup>5)</sup> G. Hartwall, *Inaug. Dissert.*, Helsingfors, (1904).

*benzoyl-formate*; however his results were as negative as those of Cohen and Whiteley.

Because of technical difficulties Fischer and Slimmer's attempts to produce a one-sided *cyanhydrine*-synthesis with *helicine*:



had at last to be given up. In the last case the apparently positive result was produced by the admixture of a strongly optically active condensation-product in the *oxy-phenyl-ethyl-carbinol* finally obtained.

Scholtz<sup>1)</sup> started with *N-methyl-α-pipecoline*, and combined *laevogyrate amyl-iodide* with it; the unattacked base however proved to be absolutely *inactive*.

In 1904 Marckwald,<sup>2)</sup> starting with inactive *methyl-ethyl-malonic acid*, obtained finally an optically active *valeric acid* in the following way.

He prepared from the first compound the *acid brucine-salt*, the solution of which was evaporated and the less soluble product separated from it. This was then heated to 170° C, *carbon-dioxide* driven off, and the *brucine* removed from the residue.

The *valeric acid* thus obtained was a mixture of the racemic and 10% *laevogyrate acid*. Tymstra<sup>3)</sup> found that the final product yields more than 25% excess of *laevogyrate acid* if heating is done in *vacuo*; the temperature must not be higher than 100°—120° C. in that case. Cohen and Patterson<sup>4)</sup> are right in their criticism when they contend that the first stage of Marckwald's process is in reality nothing but Pasteur's second fission-method of racemoids.

They compare the reaction with the case in which ordinary *racemic acid* was first resolved by *brucine*, and then the less soluble *tartrate* obtained was reduced to *brucine-malate*: in this case, after saponification, undoubtedly an optically active *malic acid* should be found. However, if Marckwald had heated the originally obtained mixture of the *brucine-salts* immediately, and in such a

<sup>1)</sup> M. Scholtz, Ber. d. d. Chem. Ges. **34**. 3015. (1901).

<sup>2)</sup> W. Marckwald, Ber. d. d. Chem. Ges. **37**. 349. (1904).

<sup>3)</sup> S. Tymstra Bzn, Ber. d. d. Chem. Ges. **38**. 2165. (1905).

<sup>4)</sup> J. B. Cohen and T. S. Patterson, Ber. d. d. Chem. Ges. **37**. 1012. (1904); W. Marckwald, *ibid.* **37**. 1368. (1904).

way that heating was stopped before the splitting-off of *carbon dioxide* was fully completed, he undoubtedly would have found an excess of the left antipode in the residue, after the *brucine* was removed from it.

An attempt of Marckwald and Meth<sup>1)</sup> to render an optical activity to *ethyl- $\alpha$ -chloro-phenyl-acetate* by heating it with two molecules of *brucine*, and to isolate the unattacked ether from the reaction-mixture, had no positive result. But when the *amide-formation* was used, the velocity of which, according to Menschutkin's investigations, is to a high degree dependent on the chemical constitution of the reacting molecules, they found that there was a considerable difference in velocity, if *l-menthyl-amine* and racemic *mandelic acid* were used in the process. Indeed the non-attacked acid appeared to be *laevogyrotory*, and therefore the ratio of the velocities  $V_a : V_l$  was about: 0,86 in this case,

If  *$\alpha$ -phenyl-ethyl-amine*:  $C_6H_5 \cdot CH(NH_2) \cdot CH_3$ , was heated with *l-quinic acid* at 165° for 4½ hours, and if the *quinate* of this base not yet transformed into *amide*, was decomposed by *Na OH*, the base finally obtained appeared to have an excess of about 3% of the *dextrogyrate* component. The ratio of the velocities, at which combination with the *laevogyrate acid* took place, was here:  $V_a : V_l = 0,88$ .

The velocity of racemisation of two compounds of the same optically active base with a left-, or righthanded acid, will also appear to be different, if they be heated above their racemisation-temperature.

Such facts were already met with in Fischer's experiments on the transformation of sugars.

Marckwald and Paul<sup>2)</sup> heated racemic *mandelic acid* and *brucine* at 150° C. for ten hours; when the molten mass, after solidification, was dissolved in water, and the acid set free by means of *sulphuric acid* and extraction with *ether*, it appeared indeed to be *dextrogyrotory*.

Since 1904 Mac Kenzie and his collaborators<sup>3)</sup> have by an

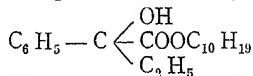
1) W. Marckwald and R. Meth, Ber. d. d. Chem. Ges. **38**. 801. (1905).

2) W. Marckwald and D. M. Paul, Ber. d. d. Chem. Ges. **38**. 810. (1905).

3) A. Mac Kenzie, Journ. Chem. Soc. London. **85**. 378, 1004, 1249. (1904); A. Mac Kenzie and H. B. Thompson, Journ. Chem. Soc. **91**. 789. (1907); A. Mac Kenzie and H. Wren, *ibid.* p. 1215. (1907); A. Mac Kenzie and H. A. Müller, *ibid.* p. 1814. (1907).

abundant series of investigations brought full experimental proof and the exhaustive demonstration of the possibility of such one-sided syntheses under the directing influence of pre-existent molecular dissymmetry,

If *l*-menthyl-benzoyl-formate was treated with ethyl-magnesium-iodide, and then the compound obtained by the aid of water:



saponified by potassium-hydroxide, the phenyl-ethyl-glycolic acid produced, appeared to be laevogyatory. If however instead of  $\text{C}_2\text{H}_5\text{MgJ}$ , the corresponding  $\text{C}_6\text{H}_5\text{MgBr}$  was used in this reaction, the benzilic acid obtained was absolutely inactive.

The *l*-menthyl-ether of pyruvic acid was reduced by Al-amalgama and a little water, and the product decomposed by alcoholic caustic potash: now a laevogyrate lactic acid resulted.

Fractional saponification of *l*-menthyl-rac.mandelate gave almost always a dextrogyrate mandelic acid; it was proved by a series of controlling experiments that the result was affected by the racemising influence of the alkali, and that the quite opposite results previously stated in many cases, could be simply explained by the shorter or longer duration of this racemising action of the saponifying base. The relative velocities of saponification of *l*-menthyl-, or *l*-bornyl-d-, resp. -*l*-mandelates by dilute hydrochloric acid, were also measured. It appeared that the *l*-bornyl-esters are saponified much more quickly than the corresponding *l*-menthyl-ethers, and that in both cases the derivatives of the dextrogyrate mandelic acid are the more rapidly saponifiable.

The following dates, obtained with a 0.07725 normal hydrochloric at 40° C, may give some impression of these differences:

Reaction-constant:		Reaction constant:	
	<i>k</i> :		<i>k</i> :
<i>l</i> -bornyl- <i>l</i> -mandelate	81,2	<i>l</i> -bornyl- <i>d</i> -mandelate	84,9
<i>l</i> -menthyl- <i>l</i> -mandelate	28.5	<i>l</i> -menthyl- <i>d</i> -mandelate	35,6
(time in minutes)		(time in minutes)	

The ratio of the velocities is here in both cases:

for the bornyl-ethers,  $\frac{V_d}{V_l} = 1,046$ ;

for the menthyl-ethers,  $\frac{V_d}{V_l} = 1,250$ .

If *fumaric acid* be transformed into the *l*-bornyl-ether, and then oxidized with *potassium-permanganate* in *acetic acid*-solution, a *laevogyrate bornyl-tartrate* was obtained, from which an also *laevogyrate tartaric acid* was set free. Better results were again obtained, when the *acid* ether of *borneol*, or the neutral ether of *menthol* were used for this purpose; and it was also proved that in using the oppositely rotating *borneol*, an excess of the *dextrogyrate tartaric acid* finally resulted.

§ 10. From these experiments the correctness of the view is proved, beyond all doubt, that a *pre-existing molecular dissymmetry has a powerful guiding influence on the chemical synthesis in which new asymmetric carbon-atoms are created*. From this the one-sided natural synthesis in plants and animals has not only become conceivable, but the contrast between the natural synthesis by the living organism and that by the chemist, as contended by vitalists, has mostly *vanished*, since the one-sidedness of natural synthesis is thus brought within the scope of chemical dynamics, it being now reduced to a merely relative *difference in reaction-velocities*.

The important investigations on catalysis by Bredig <sup>1)</sup> and his pupils during the last eight years before the war, have corroborated these ideas most thoroughly, since the analogy of chemical catalysis and the action of organic *enzymes* and *ferments* was absolutely demonstrated by them.

It has been already repeatedly stated in the preceding pages that *ferment*-, and *enzyme*-action is evidently not really a "specific" one, but merely quantitatively differing. Dakin found, that *benzyl-l-mandelate* was decomposed by *lipase* (from the liver) about 40% more slowly than the corresponding *dextrogyrate* ether. Herzog and Meier found this inequality of reaction-velocity also, when the oxidizing ferments of many fungi and moulds acted upon *d*-, or *l*-*tartaric acids*. According to Rosenthaler <sup>2)</sup>, *emulsine* produces an excess of *dextrogyrate nitrile*, if *HCN* be added to *benzaldehyde*. If the higher molecular symmetry, and

1) G. Bredig and R. W. Balcom, Ber. d. d. Chem. Ges. **41**. 740. (1908); G. Bredig and K. Fajans, ibid. p. 752. (1908); G. Bredig, Verh. d. naturwiss. Verein Karlsruhe, **25**. (1913); K. Fajans, Zeitschr., f. phys. Chemie, **73**. 25. (1910); G. Bredig and P. S. Fiske, Bioch. Zeits. **46**. 7. (1912); H. J. M. Creighton, Zeits. f. phys. Chemie **81**. 543. (1913).

2) L. Rosenthaler, Archiv. d. Pharmac. **249**. 510. (1911); Bioch. Zeits. **14**. 247. (1908); **19**. 186. (1909).



therefore the optical inactivity of matter be considered a "more probable state" than the non-superposable enantiomorphism of the optically active molecules, — a view strongly upheld by the striking tendency for auto-racemisation of optically active matter, then the materials and substances of the living world would certainly have a higher degree of instability than those produced outside the living organisms. In the light of the views mentioned here, the significance of this becomes more evident, because the matter more rapidly produced, will also be more quickly attacked in the physiological processes of the organism, and these substances will therefore be more particularly suited for its never ceasing needs. The presence of accelerating catalysts like *enzymes* and *ferments*, is absolutely necessary in these assimilation-processes, and the question may arise if it will likewise be possible to imitate the special mode of action of these catalysts by processes such as met with in one-sided synthesis?

In point of fact, the experiments just referred to, have proved this to be beyond all doubt.

Bredig and Fajans were able to show that the use of *laevogyrate nicotine* as a solvent with catalytic action in the decomposition of *d*- and *l*-campho-carboxylic acids, had the effect that the *dextrogyrate* acid was *more rapidly decomposed* into *camphor* and *carbon-dioxide* than the *laevogyrate* antipode. On the other hand, the decomposition-velocity of both isomerides appeared to be identical in optically inactive solvents, such as *aniline* or *acetophenone*.

The following data may make this clear:

*Dextrogyrate campho-carboxylic Acid.*    *Laevogyrate campho-carboxylic Acid.*

Solvent:	Velocity-constant <i>k</i> :	Solvent:	Velocity-constant <i>k</i> :
<i>Aniline</i>	0,00676	<i>Aniline</i>	0,00663
<i>Acetophenone</i>	0,00128	<i>Acetophenone</i>	0,00123
<i>l-Nicotine</i>	0,00488	<i>l-Nicotine</i>	0,00434

The velocity of decomposition of the *dextrogyrate* acid is about 13% greater than that of the *laevogyrate* acid. Also the enormously accelerating influence of basic solvents such as *aniline*, in comparison with that of different neutral solvents like *acetophenone*, is strikingly proved by these figures: a fact which beyond all doubt must be connected with the intermediate formation of a compound between the basic solvent and the acid under consideration.

The experiments, in which the *campho-carboxylic acids* were dissolved in *nitrobenzene* or *acetophenone* and then a smaller quantity of *l-nicotine* was added, demonstrated that the effect of *nicotine* is not to be attributed to the fact that it has merely the function of a solvent. They then found:

*d-acid* + *l-nicotine*, dissolved in *nitrobenzene*:  $k = 0,00302$ ; in *acetophenone*:  $k = 0,00277$   
*l-acid* + *l-nicotine*, dissolved in *nitrobenzene*:  $k = 0,00279$ ; in *acetophenone*:  $k = 0,00233$ .

The *dextrogyratory acid* in *nitrobenzene* decomposed with a velocity of about 8 % greater than the *laevogyratory acid*; in *acetophenone* with a speed about 17% greater. This result proves again that the nature of the solvent has an appreciable influence on the difference of velocities for both antipodes.

Fajans investigated in the same way the velocity of decomposition of the *campho-carboxylic acids* and *bromo-campho-carboxylic acids*.

Besides *nicotine*, this author studied the influence of *quinine* and *quinidine*, when added in small quantities to a solution of the acids in *acetophenone*.

At 70° C. the ratio of the velocity-constants of the right and lefthanded antipodes was found to be:

$$\varepsilon = \frac{k_d}{k_l} = 1,19, \text{ in the case of } \textit{nicotine},$$

whereas in *acetophenone* at 75° C. it was

$$\text{for } \textit{quinine}: \varepsilon = 1,46$$

$$\text{for } \textit{quinidine}: \varepsilon = 1,46.$$

In the catalytic action of *quinine*, half of the *dextrogyrate acid* originally used was decomposed in 92 minutes, whereas the *left acid* dwindled to half its original amount in 135 minutes. If instead of *quinine*, *quinidine* were used as a catalyst, the *dextrogyrate acid* was lessened to half its amount in 107 minutes, whereas the *laevogyratory acid* dwindled to half its original concentration in 157 minutes.

The speed of the reaction of the *inactive acid* is intermediate between the values obtained for the optically active components; it is difficult to say whether or not it may be concluded from the data, that there is still some *racemised acid* really existent in the solution, or that it is completely dissociated into its components.

In the case of the *bromo-campho-carboxylic acids*, the righthanded

antipode is decomposed more rapidly, when *quinidine* is the catalyst, whereas the lefthanded antipode is on the contrary more readily split up when *quinine* is present in the solution.

If the decomposition be stopped before complete fission of the acid has been reached, the inactive acid originally used will show an optical activity.

When *quinine* was used as catalyst, in *acetophenone* as a solvent, the portion of the acid not yet decomposed had become *dextro*-gyratory (an excess of 14% of the *d*-acid being present after a heating for 168 minutes), while the *camphor* produced in this reaction was *laevogyratory*. But if under the same circumstances (75° C.) *quinidine* were used as catalyst, the unattacked acid had after 186 minutes of heating become *laevogyratory*, while the *camphor* appeared to be *dextrogyrate*.

In these experiments the active bases are neither consumed in a detectable quantity, nor does there exist a stoichiometrical relation between the quantities of the bases added and that of the acid attacked; there is merely an *accelerating* influence, so that the function is absolutely comparable with that of organic *enzymes* or *ferments*. Indeed, here we have to deal with the complete analogue of the action of the organic catalysts, and their remarkable "specificity".

Bredig and Fiske treated *benzaldehyde* with *HCN* in the presence of *l*-*quinine* or *d*-*quinidine*; the reaction took place in *chloroform* as solvent. The base was removed by extracting the solution by shaking it with 4-normal *sulphuric acid*, and the *mandelic acid* thus obtained, when tested, appeared to be in reality optically active. If the *laevogyratory quinine* were used as a catalyst, the acid was *dextrogyratory*, whereas with the *dextrogyrate quinidine*, it was found to be *laevogyratory*. These facts remove all doubt as to the fact that the remaining traces of adhering base cannot be the cause here of the optical activity observed.

Since the experiments of Marckwald and Paul, which are in some respects perhaps comparable with those mentioned here, never has the remarkable analogy of specific *enzyme*-action, and that of much more simply built catalysts such as *quinine*, *quinidine*, etc., been brought to the fore in such a striking way. Beyond all doubt we have to deal in both cases with the *unequal velocities* of decomposition of the compounds formed intermediately between the two antipodes and the accelerating, dissymmetrical catalysts.

If only the ratio of both velocity-constants be supposed to *far surpass unity*, the one-sidedness of *enzyme-action* will now be fully conceivable, as there is an equilibrium between the free acids and bases and the salts formed by their combination, and as the quantities characteristic of the state of equilibrium are inversely proportional to the constants of the reaction-velocities of both opposite reactions. It follows that the specificity of the *enzyme-* and *ferment-action* is really of a *quantitative*, rather than of a *qualitative* nature, it being founded on an appreciable difference in reaction-, or rather in decomposition-velocity of the intermediately formed combinations between the substance attacked and the dissymmetrical catalysts.

§ 11. After all that has been done hitherto in this field of research, we can therefore safely claim to have a much clearer insight into the significance of the one-sided synthesis of the living organism. The occurrence of optically active substances during that synthesis in living bodies, finds its explanation in the fact that natural synthesis can *never* lead to a state of *completed* chemical equilibrium, the produced substances being continuously withdrawn from and used by the organism to suit its physiological needs. In connection with the fact that such chemical processes commonly proceed in several *stages*, which cannot represent states of finished equilibrium, but are only consecutive steps in the whole chain of events, — the apparent contrast between natural and artificial synthesis is explained by the mere fact that no highest degree of mechanical stability, and therefore no highest degree of symmetry, can be expected in the synthesis performed by the living organism. In natural synthesis rather a preference appears for the formation of *metastable* intermediate products, because the whole process of life is based upon the instability of the conditions of the moment, and their uninterrupted change. Metastable products generally act much more energetical than the stable phases under the same conditions, and their assimilation will therefore occur more easily and more rapidly in the physiological processes of the living organism. Moreover, as soon as such a lower symmetrical molecule, different from its mirror-image, has once been created within the living cell, the one-sidedness of further synthesis is not only fully conceivable, but it is even a necessity, as we have seen above. The asymmetric synthesis can no longer be considered as being the prerogative of life; and this

line of demarcation traced by vitalists, can also be considered to have disappeared, at least in principle. For although, as already stated, the one-sidedness of natural synthetical processes is no longer to be regarded as inconceivable, and although even these facts are now brought completely within the scope of our laboratory-experiments, the great fundamental problem of performing a *total* asymmetric synthesis directly, remains yet to be solved.

It was Meyer<sup>1)</sup> who in 1903 again laid stress on this side of the question, and who pointed quite rightly to the insufficiency of the experiments made up till now for this purpose. His remarks as to the special symmetry of the magnetic field in Boyd's experiments are absolutely justified. With a magnetic field *alone*, any result of this kind can *never* be expected; for the homogeneous magnetic field has the symmetry  $C_{\infty}^H$  (Chapter V), and thus has a plane of symmetry perpendicular to its lines of force. If however, as proposed by Meyer, a polarised lightbeam, having the symmetry  $C_2^V$  travel through the magnetic field in a direction parallel to its lines of force, the superposition of these two phenomena is equivalent to the production of a physical cause compatible with the symmetry of the group  $C_n$  where  $n$  is  $\geq 2$ . Indeed, the magnetic rotation of the plane of polarisation of such a ray as is really observed in this case, is a phenomenon having the symmetry  $C_{\infty}$ . This symmetry is *not* qualified by the existence of any symmetry-element of the second order, and in this case, when the phenomenon considered may be a cause of chemical action, the result might eventually be such as desired. The same is true, — and in the authors opinion with perhaps a greater chance of success, — if a magnetic field ( $C_{\infty}^H$ ) be superposed on an electric field ( $C_{\infty}^V$ ), whether it be an electrostatic field or an electric current.

The question occupying us here must therefore be treated experimentally, either by searching for an intrinsically *photo-chemical* reaction, or for an *electrolytical*, or more in general: for an *electro-chemical* process in which a *new* asymmetric carbon-atom is produced in the molecule, and which reaction, in the way described above, can be dissymmetrically arranged, i.e. under circumstances,

<sup>1)</sup> J. Meyer, Jahresber. der Schles. Ges. f. vaterl. Kultur, IIe Abt., Dez. (1903), p. 34; Chem. Zeitg. (1904). p. 41.

the complex of which forms a system of causes non superposable with its mirror-image. Indeed, if we compare these postulations with the conditions hitherto created in the very few direct experiments of this kind, we must come to the conclusion, that no serious and well thought-out attempts in this direction must be neglected in future.

Some of the plans to be followed have already been shortly indicated in Chapter V; and some of these experiments have now been started in the author's laboratory. But no experiments in other laboratories should be left untried, as this problem is an extremely important one for the general development of our scientific conceptions in this sphere of research, and the experimental evidence brought by others can only be adopted gratefully, as a help in overcoming the very great experimental difficulties of these investigations.

All attempts, even those well thought-out, to bring about a *total* asymmetric synthesis directly, have up till now only met with negative results.

In Meyer's experiments the *benzoyl-formate* of *laevogyrotory amyI-alcohol* was reduced to the corresponding *mandelate* by *sodium-amalgama*, in a magnetic field of 180 C. G. S., while a beam of polarised light passed through the solution parallel to the lines of force. The result was that only *racemic mandelic acid* could be obtained. This negative result cannot be wondered at, as the experiment is badly conceived.

For this reduction does *not* really depend on the presence of the magnetic field, nor on that of the light-energy; it is *no* photochemical reaction in which the luminous energy is the *necessary* condition for starting it; and moreover the strength of the magnetic field applied, is much too small for such experiments.

Henle and Haakh<sup>1)</sup> therefore tried a characteristic photochemical process: the decomposition of some *carboxylic acids* by light under production of *carbon-dioxide*, which reaction is appreciably accelerated by the presence of *uranyl-salts*, and — as the author stated, — in many cases by that of *ferri-salts* too<sup>2)</sup>. The desired dissymmetry of the physico-chemical causes was obtained either by rotating the plane of a beam of polarised light by a magnetic field, or by producing circularly polarised light with the

1) F. Henle and A. Haakh, Ber. d. d. Chem. Ges. 41. 4261. (1908).

2) F. M. Jaeger, Proceed. Kon. Ak. van Wet. Amsterdam, 14. 342. (1911).

aid of a *mica*-lamella of  $\frac{1}{4}\lambda$ , as often used in optics. In this way the transformation of *methyl-ethyl-cyano-acetic acid* into *methyl-ethyl-aceto-nitrile*, and that of symmetrical *dichloro-dimethyl-succinic acid* into *dichloro-dimethyl-propionic acid*, was studied by them. The results were negative, and only optically inactive products were obtained in the reactions.

The experiments of Rosenthal,<sup>1)</sup> who claimed to have hydrolysed highly complicated *carbohydrates* in an oscillatory electromagnetic field, are *not* confirmed by later investigations, and may therefore be passed over here.

§ 12. However an *indirect* proof of the possibility, — even of the *necessity*, — of such a *total* asymmetric synthesis on earth, has been given by the reasonings, and by some experiments, of Byk.<sup>2)</sup> His suppositions are based on a number of facts which were previously established by other investigators, and which, when combined, seem to be adapted to prove the possibility that there is such a one-sided formation of optically active matter, as searched for in the problem under consideration. He points out that a supposition as made in the discussion by Japp a.o., previously mentioned, *never* can explain the one-sidedness of natural synthesis. Such a separation by mere chance, or by some accidental cause such as whirl-winds, etc., of an optically active germ from an externally-compensated mixture, created by spontaneous crystallisation, as it was supposed by some of the authors mentioned, would in the immeasurable periods of geological evolution, even under the best conditions only have led to an externally compensated, or a *pseudo-racemic* world, but never to the one-sided material world we actually have. No other causes can be taken into account therefore when considering the origin of the first optically active substance, than those physical causes outside the range of life, which are dissymmetrical in themselves, in the sense explained in Chapter V.

Now Byk tries to prove that such a one-sided cause has existed on earth for immeasurable ages, and more particularly, that the source of photochemical energy having the special dissymmetry necessary for such total asymmetric synthesis, was the circularly polarised light, reflected, — while under the influence

1) J. Rosenthal, Sitzber. Akad. d. Wiss. Berlin (1908), I. p. 20.

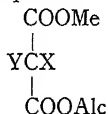
2) A. Byk, Ber. d. d. Chem. Ges. **37**. 4696. (1904); Zeits. f. phys. Chemie, **49**. 641. (1905).

of terrestrial magnetism<sup>1)</sup>, — by the surface of the seas and oceans<sup>2)</sup>. He proves, that the coincidence of the wave-length, for which light-absorption is a maximum, and for which photochemical action is an *optimum*<sup>3)</sup>, also holds good, as Cotton demonstrated<sup>4)</sup>, in the case of the *cupri-alkali-salts* of *d*-, and *l*-tartaric acids, which absorb right- and lefthanded circularly polarised light in a *different* way. From this Byk concludes that the velocity of photochemical action must therefore be *different*, when such antipodes are attacked by circularly polarised light of oppositely directed rotation. And he proves that this must be true also for Fehling's solution, because the light-absorption of the ions in dilute solutions must, as Oswald<sup>5)</sup> also contends, be considered as independent of the presence of other ions. From this it follows as a logical consequence, that in the case of optical antipodes in an externally compensated mixture, it is possible for the chemical process to go on at different velocities, when these antipodes are attacked by circularly polarised light of a definite direction of rotation. The author tries to demonstrate that on earth really all conditions have always been fulfilled for causing a constant excess of circularly polarised light of a definite direction of rotation. The possibility of the *total* asymmetric synthesis, according to Byk's views, is therefore indirectly demonstrated, and its experimental verification is only a matter of finding out the suitable materials and experimental arrangements. This solution must therefore be sought in the field of *photochemistry*.

§ 13. It is not our intention to consider in detail the different ways in which in the present author's opinion, the experimental solution of the problem under consideration should be sought.

A single suggestion however may find its place here.

From the substituted *malonic acids* of the type:  $CXY(COOH)_2$  the ether-salts of the composition:



1) H. Becquerel, Compt. rend. de l'Acad. d. Sc. Paris, **108**. 997. (1899).

2) J. Jamin, Compt. rend. de l'Acad. d. Sc. Paris, **31**. 696. (1850).

3) J. M. Eder, Sitzb. Akad. d. Wiss. Wien, **90**. 1097. (1885); **92**. 1346. (1885); **94**. 75. (1886).

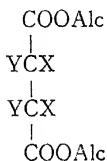
4) A. Cotton, Ann. de Chim. et Phys. (7). **8**. 347. (1896).

5) W. Ostwald, Zeits. f. phys. Chemie. **9**. 579. (1892).



can be prepared, the aqueous solutions of which will of course contain an equal number of dextro- and laevogyrate ions.

Now if with a sufficient current-density, an electrolysis of this solution is started, both these ions will split off *carbon-dioxide* to form an ether of the type:



and this decomposition, going on with equal velocities for both kinds of stereometrical configurations, will therefore necessarily lead to an optically *inactive* product.

If however this electrolysis be started in a very strong magnetic field, the lines of force of which are parallel to the direction of the current, and especially, if the metal *Mc* be so chosen as to increase the magnetic susceptibility of the solution, there *may* be a good chance that under these dissymmetrical conditions, the electrochemical decomposition of both enantiomorphously related kinds of ions *no* longer occurs with the same velocity. In that case an optically active product might be obtained, if the process be stopped before the decomposition of the substance present is completed, and an excess of one of the optically active components of the ether might be found in the product finally obtained.

Experiments of this kind, especially with *ferric* salts of organic acids, have already been started.

§ 14. Our ideas concerning the problem of asymmetric synthesis in nature, have been much changed during the last decades.

Continual research leads us to believe that the hope need not be given up of overcoming within a not too distant future all experimental difficulties, and the dynamics of the asymmetrical synthesis will then be as accessible to us, as those of our common laboratory-processes.

If these experiments should some day have a real positive result, we shall then completely have solved one of the most fundamental riddles in the chemical and biological sciences, and we shall effectually have contributed to the final understanding of one of the most vexing phenomena which have puzzled scientists

ever since they have been able to think of problems on this level.

At the same time we shall have gained a clearer insight into the true significance and the value which the principle of symmetry has for the scientific description of the living and inanimate worlds, thus contributing most effectually to the never ceasing efforts of our race to increase our knowledge of the wonderful and mysterious ways of that greatest of artists: Nature.



## ERRATA.

- Page 7, fourteenth line from bottom: representents; read: represents.
- „ 13, sixteenth line from bottom:  $360^\circ$ ; read:  $450^\circ$ .
- „ 18, Note 1), fourth line from top: thought; read: through.
- „ 21, fifteenth line from top: inversion; read: inversion-.
- „ 27, seventh line from bottom:  $L_{3,4}$ ; read!  $OL_{3,4}$ .
- „ 28, fifth line from top: with out; read: without.
- „ 28, seventh and eighth lines from top: over; read: through.
- „ 29, seventh line from bottom: proceeding; read: preceding.
- „ 31, Note, fifth line from bottom: *Wulff*; read: Wulff.
- „ 33, fourteenth line from top: als; read: also.
- „ 34, nineteenth line from top:  $C^n$ ; read:  $C_n$ .
- „ 39, seventh line from top: Figure 31; read: Figure 3r.
- „ 41, eleventh line from bottom: of intersection; read: of intersection.
- „ 42, third line from top: Ind, eedthese; read: Indeed, these.
- „ 59, eighteenth line from top: *Triglogin*; read *Trichlogin*.
- „ 60, Fig. 65. This figure must be reversed.
- „ 114, twelfth and thirteenth lines from top: parallelograms; read: parallelograms.
- „ 115, twentieth line from top: length; read: lengths.
- „ 117, first line from top: he; read: the.
- „ 122, eighteenth line from bottom: complex-molecule; read: complex molecule.
- „ 136, sixth line from top: 1916; read: 1906.
- „ 158, Notes, fourth line from bottom: intimate lyconnected read: intimately connected.
- „ 160, ninth line from top: cannot maintained; read: cannot be maintained.
- „ 168, third line from bottom: retarded; read: retarded.
- „ 170, figure 133 must be turned through  $90^\circ$ , the vertical striation of the one cube-facet becoming horizontal.
- „ 172, twelfth line from top: crystalform; read: crystal-form.
- „ 173, figure 134 must be turned  $30^\circ$ , so that the Roman ciphers are placed in normal position.
- „ 186, eighteenth line from top: plance; read: plane.
- „ 186, fourteenth line from bottom: -rays; read: -rays.
- „ 194, tenth line from top: conclusively, that tendency; read: conclusively that the tendency.

Page 194, eleventh line from bottom: emphasised; read: emphasized.

„ 209, Note: 19; read: 20.

„ 227, fourth line from top: repidly; read: rapidly.

„ 235, Note: after 18. 49. (1915); insert: 20. (1917).

„ 239, third line from top: accidently; read: accidentally.

„ 240, Note: 19. (Aug.); read: 20. (June).

„ 241, fifth line from top: nothwithstanding; read: notwithstanding.

„ 242, Note: second line: 19.; read: 20.

„ 243, fifth line from top, after *preservation of*, insert: *the existent*.

„ 243, eleventh line from top: triclincipedal; read: triclinic-pedal.

„ 243, Note: 19., read: 20.

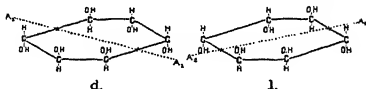
„ 244, Note, first line: Ladenburg.; read: Ladenburg.

„ 244, Note, fourth line: separated in; read: separated into.

„ 246, twelfth line from top: *here*; read: *here*.

„ 249, Note, first line:  $D_2$ ; read:  $D_2$  or  $C_2^V$ .

„ 251, third line from top; the formulae must be read:



„ 252, sixth line from top: Class; read: class.

„ 253, eleventh line from top:  $\left[ \text{Co} \begin{smallmatrix} (\text{OH})_3 \\ (\text{NH}_2)_4 \end{smallmatrix} \right]$ ; read:  $\left[ \text{Co} \begin{smallmatrix} (\text{OH})_2 \\ (\text{NH}_3)_4 \end{smallmatrix} \right]$ .

„ 255, twelfth line from top: isomeric.; read: isomeric

„ 255, eighth line from bottom: athough; read: although.

„ 256, fifth line from top: as; read: us.

„ 258, fourteenth line from top: Pasteurs's; read: Pasteur's.

„ 258, first line from bottom: question however; read: question, however.

„ 261, Fig. 168: Optically; read: optically.

„ 261, Note: 19; read: 20.

„ 263, sixth line from top: Van 't Hoff—le Bell's; read: Van 't Hoff—  
Le Bel's.

„ 264, Note, seventh line: 19; read: 20.

„ 266, eighth line from top:  $\text{Na Cl O}_3$ ; read:  $\text{NaClO}_3$ .

„ 266, sixth line from bottom: Notwithstanding; read: Notwithstanding.

„ 273, fifth line from top: The *H* of; read: The *H*

„ 275, tenth line from bottom: came; read: come.

„ 296, thirteenth line from bottom: *Acid*; read: *acid*.

„ 299, third line from top: te; read; the.

# ALPHABETIC INDEX.

OF

## AUTHORS AND SUBJECTS.

*In using this Alphabetic Index it must be kept in mind that prefixes such as: ortho-, meta-, para-, cis-, trans-, d-, l-, rac., etc., have been disregarded in the alphabetic sequence of the words. The names of authors are spaced; the names of living objects and species are printed in italics. The numbers indicated refer to the corresponding pages of the book.*

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